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# PHOTOELECTRIC CELLS

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*First published in 1946*

## PREFACE

THIS monograph is entirely devoted to photoelectric cells of the emission type, as distinct from cells of the barrier-layer and photo-conducting types. A brief survey of the principles of photoelectric emission (Chapters I and II) is followed by a more detailed description of the manufacture and properties of photocathodes (Chapters III and IV). In Chapters V to VII an account is given of vacuum, gasfilled and multiplier photocells and their relative advantages and limitations. The final Chapter VIII, dealing with applications of photoelectric cells, is confined mainly to problems of a purely photoelectric nature as distinct from circuit and design problems.

The author acknowledges with thanks the very helpful advice and suggestions he received from Mr. C. R. Bannister, B.Sc., F.C.I.P.A., A.M.I.E.E., and Dr. K. A. R. Samson.

A. S.

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## CHAPTER I

## HISTORICAL INTRODUCTION

LIKE many important physical phenomena, the photoelectric effect was discovered as a by-product of an investigation concerned with an unrelated subject by a man of genius who realised the significance of a chance observation. In 1887 H. Hertz [23] found during his experiments on electrical resonance that the length of the spark, induced by a primary spark, between the electrodes of a secondary spark gap, was reduced if the secondary electrodes were shielded from the light of the primary spark. The fact that a shield made of glass reduced the length of the secondary spark while a quartz shield had no effect indicated that this 'photoelectric effect' was caused by ultra-violet radiation and not by visible light. Hertz proved this conclusion by using an independent ultra-violet light source and made the further observation that the effect is most marked when the negative electrode of the secondary spark gap is exposed to the radiation.

Stimulated by Hertz's experiments, Hallwachs [21] observed in 1888 that an electrically charged Zinc electrode loses its charge when exposed to ultra-violet radiation if the charge is negative, but is able to retain a positive charge under the same conditions. In 1889 Elster and Geitel [12] discovered a photoelectric effect caused by visible light, by using the alkali metals Potassium and Sodium for their experiments in the place of Zinc. They produced the first photoelectric cell by evacuating a glass bulb containing two electrodes, firstly, the 'cathode', consisting of alkali metal, and secondly the 'anode' which was maintained at a positive potential in order to collect the negative charges released by light from the cathode.

It must be remembered that all the experimental work so far described was carried out before the existence of



the electron was known. After J. J. Thomson's [43] discovery of the electron in 1897 it was soon realised that the photoelectric effect was caused by the emission of electrons under the influence of radiation. The fundamental theory of photoelectric emission was put forward by Einstein [11] in 1905 on the basis of Planck's quantum theory (1900). In the following two chapters the relationship between light and photoelectric emission and the explanation for this relationship by Einstein's theory will be described in greater detail.

## CHAPTER II

### THEORY OF PHOTOELECTRIC EMISSION

#### (A) RELATIONSHIP BETWEEN RADIATION AND PHOTOELECTRIC EMISSION

A THEORY of photoelectric emission has to explain the relationship between, on the one hand, the two essential properties of radiation, i.e. intensity and wavelength, and, on the other hand, the number of released photoelectrons (in other words, the current collected by the anode of a photoelectric cell) and the energy of the photoelectrons. Of these four terms: intensity of radiation, wavelength of radiation, photoelectric current, and energy of electrons, only the last one requires a few words of explanation. The energy of a moving electron is given by the product  $eV$ , where  $e$  represents the electronic charge and  $V$  the negative potential which the electron can overcome owing to its kinetic energy. In practice it is not convenient to express the energy of an electron in units of energy (for instance, in watt-secs. if  $e$  is expressed in coulombs and  $V$  in volts), because we are usually not so much interested in the value of the energy as in the potential corresponding to this energy. It is therefore customary to speak about electrons of, say, 100 volts energy or 100 volts velocity, although, obviously, the potential has the dimension of neither energy nor velocity. However, if the potential  $V$  is known, the values for energy and velocity are easily derived as follows: The energy is obtained, as already mentioned, by multiplying the potential  $V$  by the (constant) value of the electronic charge  $e$ . The velocity  $v$  can be obtained by expressing the energy of the moving electron in mechanical terms. The kinetic energy  $\frac{1}{2}mv^2$



(where  $m$  is the mass of the electron) is equal to the energy expressed in electrical terms. Hence

$$\frac{1}{2}mv^2 = eV \text{ and } v = \sqrt{\frac{2eV}{m}}$$

It can be seen from this equation that the velocity is a function merely of the potential  $V$  because both  $m$  and  $e$  are universal constants.

From the foregoing it is clear that if we want to know the energy or the velocity of electrons released from the cathode of a photoelectric cell we have to measure the negative potential which they can overcome. If we apply to the

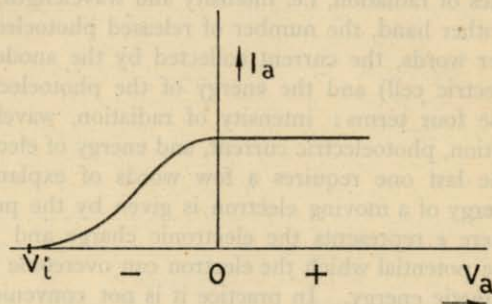


FIG. 1

anode of a photocell a comparatively high negative potential of, say,  $-10$  volts it is found that no electrons are collected by the anode; in other words, the photoelectrons all have a 'velocity' or 'energy' of less than  $10$  volts. If we gradually vary the anode potential from  $-10$  volts through zero to positive values, we obtain a curve of the type shown in Fig. 1. In this Figure the anode potential  $V_a$  is plotted on the abscissa and the photoelectric current  $I_a$ , representing the number of electrons collected by the anode, on the ordinate. It can be seen that the photocurrent starts at a definite negative potential, indicated by  $V_i$ , and rises to reach a constant maximum at  $V_a = 0$  volts. This means

that electrons are leaving the cathode with a velocity varying between  $0$  volts and the numerical value of  $V_i$ . At  $V_a = 0$  all the emitted electrons reach the anode, hence the curve does not rise any further for positive values of  $V_a$ . (It will be shown later that in practical photocells this constant value of  $I_a$  is not reached at  $V_a = 0$ , but at present we are only concerned with ideal conditions.)

Returning to the actual subject of this chapter, we can see that by varying the intensity and the wavelength of the light incident on a photoelectric cathode, and by measuring in each case the increase of the photoelectric current with rising anode potential, series of curves of the type of Fig. 1 will be obtained. As  $V_i$  is a measure of the maximum energy of the photoelectrons and  $I_a$  corresponds to the number of emitted electrons, curves representing the changes of  $V_i$  and  $I_a$  as a function of intensity and wavelength of the incident light will indicate the relationship between light and photoelectric emission.

A great number of experiments have been carried out to measure the change of the photoelectric current with varying negative anode potential under various conditions of illumination, but great experimental difficulties affect the accuracy of such measurements [3]. One difficulty consists in establishing with precision the value of  $V_i$  because of the minute currents that have to be detected at the point where the curves approach the abscissa. A further error is often caused by photoelectric emission from the anode, since at negative anode potentials photoelectrons emitted from the anode will be collected by the cathode and this photocurrent in the 'wrong direction' will falsify the measurements. It is difficult to avoid photoelectric emission from the anode because all metallic electrodes are more or less photoelectrically sensitive, and it is almost impossible to shield the anode entirely from the light incident on, or reflected by, the cathode.

However, it is outside the scope of the present monograph to describe these experimental problems and their



solutions in detail, and in the following we shall confine ourselves to a discussion of the results obtained from the most reliable experiments. If we take measurements with light of constant wavelength (preferably monochromatic

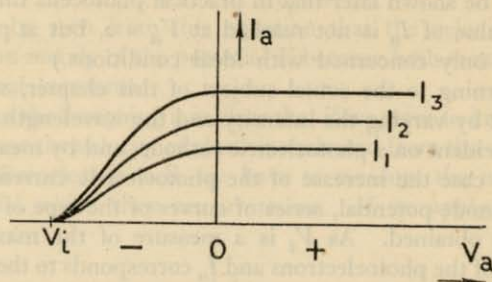


FIG. 2

light) and varying intensity we arrive at a series of curves as shown in Fig. 2. The curves are marked  $I_1$ ,  $I_2$  and  $I_3$  with increasing light intensity. The fact that all the curves converge towards the same point  $V_i$  of the abscissa means

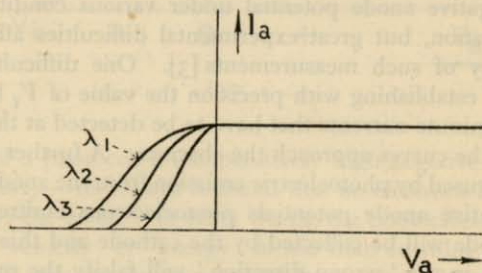


FIG. 3

that the maximum velocity of the photoelectrons is the same for all light intensities. The number of the electrons, however, increases with the light intensity and quantitative experiments show that the photoelectric current is actually directly proportional to the light intensity.

If we now keep the light intensity constant and change

the wavelength of the light we obtain the series of curves shown in Fig. 3. In this case all the curves converge towards the same point on the ordinate (this is only strictly true if the sensitivity of the cathode is constant within the considered wavelength range), but the maximum velocity of the electrons, represented by the greatest negative anode potential which they can overcome, increases as the wavelength is being reduced. In Fig. 3 the curves are marked  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  with increasing wavelength.

From the above described experimental results the following conclusions can be drawn:

- (1) The velocity of the photoelectrons is independent of the intensity of the light.
- (2) The photoelectric current, i.e. the number of photoelectrons, is proportional to the intensity of the light.
- (3) The velocity of the photoelectrons depends on the frequency (wavelength) of the light in such a way that the maximum velocity increases with increasing frequency (decreasing wavelength) of the light.

These three facts are satisfactorily explained by Einstein's theory, which will be the subject of the next section.

#### (B) EINSTEIN'S THEORY OF THE PHOTOELECTRIC EFFECT

According to the Quantum Theory of Planck, light is emitted and absorbed in discrete units of energy called light quanta or photons. The magnitude of each photon is given by the product  $h\nu$ , where  $h$  is a universal constant, 'Planck's Constant', and  $\nu$  is the frequency of the light which is emitted or absorbed. If photoelectric emission takes place the fundamental process, according to Einstein, consists of a quantitative conversion of the energy of photons into electronic energy. Therefore the photoelectric effect caused by a single photon is represented by the following equation:

$$eV = h\nu \quad . \quad . \quad . \quad (I)$$



Equation (1) explains the experimental results described in the preceding section. Greater light intensity means *more* photons but not *larger* photons; these will produce *more* photoelectrons but not electrons of *greater energy*. Therefore the velocity of the photoelectrons is not affected by the light intensity, while the photoelectric current is proportional to the light intensity.

On the other hand, greater frequency of the light means greater energy  $h\nu$  of the individual photons, and consequently the energy  $eV$  of the released photoelectrons increases with the frequency. When dealing with light we are more familiar with wavelength than with frequency, hence by making use of the equation  $\nu = \frac{c}{\lambda}$  (in which  $\lambda$  denotes the wavelength of the light and  $c$  the velocity of light) we can transform (1) into:

$$eV = hc \times \frac{1}{\lambda} \quad (2)$$

In this equation the factors  $e$  (electronic charge),  $h$  (Planck's constant) and  $c$  are universal constants. This means that we can use the equation to determine the velocity  $V$  of a photoelectron produced by a photon of light of known wavelength  $\lambda$ . By substituting the numerical values [6]

$$e = 4.805 \times 10^{-10} \text{ c.s.u.}$$

$$c = 2.99774 \times 10^{10} \text{ cm./sec.}$$

$$h = 6.622 \times 10^{-27} \text{ erg-sec.}$$

we obtain the simple equation

$$V = \frac{12,000}{\lambda} \left( \text{the exact value is } V = \frac{12,394}{\lambda} \right) \quad (3)$$

if  $V$  is measured in volts and  $\lambda$  in Angstrom units ( $1 \text{ \AA} = 10^{-8} \text{ cm.}$ ).

The range of visible light extends approximately from 4,000  $\text{\AA}$  (extreme violet) to 7,600  $\text{\AA}$  (extreme red) (see Fig. 15, page 55). Therefore the velocity imparted to

photoelectrons by visible light lies, according to equation (3), approximately between 1.6 volts (for red light) and 3.0 volts (for violet light). However, the electrons are not emitted into the vacuum with the velocity calculated from (3) because, as is well known from the thermionic emission of electrons, a moving electron can only leave a solid body if it has sufficient energy to overcome the attracting surface forces. Consequently the electrons lose some of their original energy, the amount depending on the nature of the electron-emitting substance or, more accurately, on the nature of the surface of this substance. If we express the loss of energy of the electrons in volts, the velocity of the electrons after leaving the surface will be:

$$V = \frac{12,000}{\lambda} - \phi \quad (4)$$

$\phi$  is usually called the 'work function' and is for all substances of the order of 1 to 5 volts. It is obvious that, in order to emerge into the vacuum, the velocity of a photoelectron must satisfy the equation:

$$V \geq 0$$

For the minimum value of  $V = 0$  we can derive, with the help of equation (4), the maximum value for  $\lambda$ :

$$\lambda_0 = \frac{12,000}{\phi} \quad (5)$$

$\lambda_0$  is called the 'threshold wavelength' and represents the longest wavelength which can release photoelectrons from a surface with the work function  $\phi$ . From (5) it can be seen that  $\phi$  must be smaller than 3 volts if visible light is to produce photoelectric emission. Equation (5) is of great importance, not only for the determination of the threshold wavelength of a substance of known work function, but also because it enables us to calculate the work function of a surface if  $\lambda_0$  has been found by experiment. The values for  $\phi$  thus obtained are, within the accuracy of the measurements, identical with those derived from thermionic emission from Richardson's equation.



If the velocity of photoelectrons were solely determined by equation (4) we should expect monochromatic light to produce photoelectrons of only one velocity, namely, that derived from the equation by substituting the numerical values for  $\lambda$  and  $\phi$ . In reality, the velocity thus calculated is that of the fastest electrons only and all velocities between this maximum and zero occur, as can be seen from Figs. 1, 2 and 3. The explanation for this spread of velocities is a simple one: the light falling on the sensitive photocathode is absorbed within the first few hundred atomic layers. The photoelectrons released near the surface will be able to leave the surface with the velocity calculated from equation (4), but the electrons produced in deeper layers are likely to suffer collisions with other electrons and particles on their way to the surface, with the result that they are likely to lose some of their initial energy and to arrive at the surface with a reduced velocity. It should be emphasised that, while the loss of velocity caused by the work function is the same for all electrons leaving a particular photocathode, the additional loss due to collisions within the cathode material varies according to the depth at which the electrons are released.

### (C) CONDITIONS FOR PHOTOELECTRIC EMISSION

Einstein's theory, as expressed by equations (4) and (5), in combination with some general physical considerations, enables us to formulate some essential conditions which have to be fulfilled if a substance is to be photoelectrically sensitive to visible light. In the following we will discuss the four most important conditions.

(1) *Adequate absorption of light.* An obvious condition for the conversion of photons into electronic energy within a substance is that the photons should be absorbed by the substance. (Though photoelectric emission without light absorption is impossible, absorption of light does not, of course, necessarily lead to photoelectric emission.) This first condition excludes, or at least severely limits, the use

of two groups of materials as photoelectric emitters, i.e. transparent and highly reflecting substances. Examples of the first group are materials like glass, mica and all colourless salts, while the main representatives of the second group are the metallic elements, which have reflection coefficients exceeding 90%.

(2) *Low atomic binding forces.* In view of theoretical considerations, which we cannot here discuss in detail, 'free'

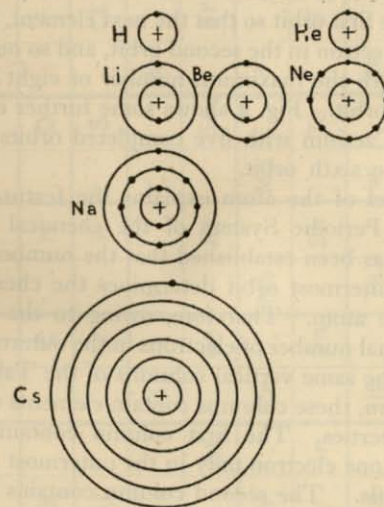


FIG. 4

(or 'conduction') electrons are unable to absorb photons if the law of the conservation of momentum is to be maintained. Hence, the electrons released by light must be 'bound' electrons, but it is obvious that the smaller the force by which the electron is bound to the atom the easier it will be to detach the electron from the atom. According to the latest theoretical development there is no longer any distinct demarcation line between 'bound' and 'free' electrons, but for our purpose it is sufficient to imagine the







outermost occupied orbit is removed from the nucleus the smaller is the force exerted by the nucleus on the electron(s) in this orbit. Hence, the binding force should decrease from the top to the bottom of the Table of the Periodic System. Secondly, as the number of electrons in the outermost orbit is decreasing from the maximum number for the particular orbit to one, the attracting forces of the positive nucleus penetrating to this orbit are reduced. This means that the electrons should be less firmly bound as we go from the right to the left in the Periodic Table. Combining these two conclusions, it is to be expected that each alkali metal atom, having only one electron in the outermost orbit, should possess a comparatively loosely bound electron and that the alkali metal atom with the greatest number of occupied orbits, that is the Caesium atom, should part most easily with this electron.

The work required to remove an electron entirely from an atom, in other words to ionise the atom, is the ionisation energy  $E_i$  and can be expressed in volts, in analogy to the work function. The ionisation energy of substances in the gaseous state has been determined with great accuracy from spectroscopic measurements, and the  $E_i$  values of some chemical elements are shown in Table I [6]. Despite the

TABLE I  
Ionisation Energy  $E_i$  and Work Function  $\phi$  of some  
Chemical Elements

	$E_i$	$\phi$		$E_i$	$\phi$
Li	5.4		Zn	9.4	3.4
Na	5.1	2.5	Fe	7.9	4.8
K	4.3	2.3	Ni	7.6	5.0
Rb	4.2	2.1	Mo	7.4	4.1
Cs	3.9	1.8	He	24.5	
.....					
Mg	7.6	(2.4)	Ne	21.5	
Ca	6.1	(2.3)	A	15.7	
			Kr	14.0	
			X	12.1	

fact that in photoelectric emitters we are concerned with solids for which conditions are markedly different, the absolute values of  $E_i$  for gases give us an indication of the relative values for solids. It can be seen from the Table that the conclusions of the preceding paragraph are borne out by the facts. The elements with only one electron in the outermost orbit, the alkali metals, require lower ionisation energies than any of the other elements and, furthermore, the ionisation energy decreases with growing atomic weight from Lithium to Caesium. In accordance with our expectations the alkali metal Caesium, which is farthest to the left in the bottom row of the Periodic Table, has the lowest known ionisation energy among the chemical elements.

Coming back to photoelectric emitters, we can summarise the results of the preceding considerations by stating that the second condition for photoelectric sensitivity, i.e. low atomic binding forces, is most satisfactorily fulfilled by the group of alkali metals with Caesium being the most suitable metal of the group.

(3) *Low work function.* Since we have discussed the effect of the work function on the emission of electrons in Section (B), it can be stated without further explanation that low work function is an essential condition for photoelectric emission and that, expressed more precisely, the value of the work function must be below 3 volts to produce a threshold wavelength  $\lambda_0$  (see page 9) within the visible range of the spectrum, i.e. above 4,000 Å, and below 1.6 volts if sensitivity for the *whole* visible spectrum, i.e. up to 7,600 Å, is required. The values of the work function  $\phi$  of some chemical elements can be found in the second column of Table I [6], from which it is apparent that (in agreement with the modern theory of metals) the relative figures correspond to those for the ionisation energy, i.e. small atomic binding forces are linked with low work function. (It may be mentioned in passing that the work function cannot be measured with anywhere near the same



accuracy as the ionisation energy. The measurements are based on Richardson's equation for thermionic emission and on determinations of the threshold wavelength according to equation (5) on page 9.) The alkali metals possess the lowest work functions and the minimum value is again obtained for Caesium. Therefore, substances which fulfil condition (2) are also photoelectric emitters which fulfil condition (3).

It must be emphasised at this point that in our discussion of the conditions (2) and (3) we have only considered chemical elements as distinct from chemical compounds. We shall see later that in modern photoelectric cathodes we have to deal with materials of complicated chemical structure, but by limiting ourselves to the chemical elements the fundamental facts are more easily understood.

(4) *Specific resistance of semi-conductor.* The fourth and last condition is in the nature of a compromise between two contradicting conditions. On the one hand, substances of metallic conductivity are, according to condition (1), unsuitable as photoelectric emitters because of their optical properties. On the other hand, substances of very high specific resistance (insulators) are unsuitable because electrons released by light from an insulator cannot be replaced so that a photoelectric current cannot be maintained. Hence substances of intermediate specific resistance, i.e. semi-conductors, are likely to be the best photoelectric emitters.

### CHAPTER III

#### MANUFACTURE AND PROPERTIES OF SOME TYPES OF PHOTOELECTRIC CATHODES

IN this Chapter the photoelectric cathodes which have been developed to date will be described in historical sequence. The now obsolete types will be dealt with very briefly, but more details will be given of those which are of practical importance. With regard to the manufacturing processes we shall confine ourselves in this chapter to describing how the various types of sensitive cathodes are made and how their properties can be explained by the theoretical considerations of the preceding chapters. Complete photoelectric cells and such problems as geometry of the cell, shape and position of the anode, gasfilling, &c., will be discussed later.

The two properties that determine the usefulness of a photoelectric cathode are, firstly, the relative sensitivities at various wavelengths throughout the spectrum, and, secondly, the absolute value of the sensitivity at each wavelength. The sensitivity for a particular wavelength can be expressed either in photocurrent per unit of radiated energy (for instance, in amperes per watt) or in percentage of the theoretical maximum sensitivity. The latter is achieved if each photon  $h\nu$  produces one photoelectron, in which case we speak of a 'quantum yield' of 100%. The quantum yield can be calculated for a particular wavelength by measuring the photocurrent (i.e. the number of electrons released) and the energy of the light incident on the photocathode.

To give a simple numerical example: if the light energy is measured (for instance with a thermocouple) to be 1 milliwatt and the wavelength of the light is 6,000 Å, corresponding to a velocity of the electrons of

$$V = \frac{12,000}{\lambda} = 2 \text{ volts,}$$



then the maximum photocurrent that can be produced is given by the equation

$$I_{max.} = \frac{0.001}{2} = 0.0005 \text{ amperes} = 500 \text{ microamperes.}$$

If now, for argument's sake, the actual photocurrent is found to be 5 microamperes, the quantum yield in this particular case would be 1%.

If we plot the amperes (of photocurrent) per watt (of radiant energy) values for a photocathode against the wavelength, for all wavelengths to which the cathode is sensi-

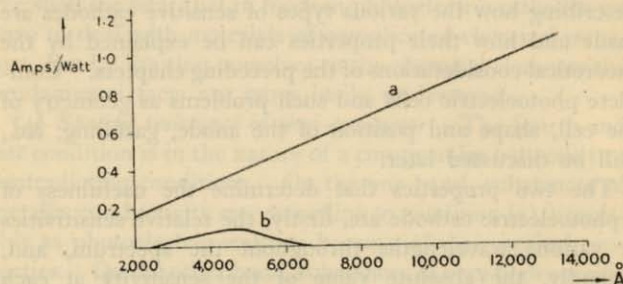


FIG. 6

tive, we obtain colour response curves of the type shown by curve (b) in Fig. 6. In this Figure curve (a) represents the response of the ideal photocathode with a quantum yield of 100%, so that the quantum yield at any wavelength is represented by the ratio of the ordinates of curves (b) and (a). The fact that curve (a) does not run parallel to the abscissa is, of course, due to the higher velocity of the photoelectrons at shorter wavelengths, because for each photoelectron released by one watt of light of 4,000 Å, two electrons of half the velocity will be produced by light of 8,000 Å (see equation (3) on page 8).

Before describing the manufacture of individual types of photocathodes it may be useful to mention that all cathodes—in common with electron emitters of the ther-

mionic type—have to be enclosed in an evacuated vessel. In the case of photocathodes this is necessary not only to ensure a long mean free path of the electrons but also to avoid chemical contamination of the alkali metals which form a component of all modern photocathodes. (The only exception is the use of rare gases at very low pressure; see Chapter VI.) It is outside the scope of this book to describe the methods of 'vacuum technique', but one limitation, imposed by the need of maintaining a high vacuum in photoelectric cells, should be mentioned. It is that all parts of the cell must stand up to a baking process at a temperature of approximately 400° C. The purpose of this heat treatment is to remove all gas molecules adsorbed by the glass walls and the metal parts, this being essential to ensure a good vacuum after the cell has been removed from the pump system.

#### (A) THE ZINC PHOTOCATHODE

As mentioned on page 1, the first substance which was found to be photoelectrically sensitive was the metal Zinc. It was also stated that Zinc is not sensitive to visible light but only to ultra-violet radiation, a limitation which is explained by the high work function of Zinc. By using the value  $\phi = 3.4$  volts (see Table I) in equation (5), we find that the threshold wavelength  $\lambda_0$  lies well below 4,000 Å, so that electrons released within the cathode by visible light are unable to leave the surface.

#### (B) THE ALKALI METAL PHOTOCATHODE

The earliest photoelectric cells which responded to visible light contained cathodes consisting of Alkali metals (see page 1). This is in agreement with our conditions (2) and (3) for photoelectric emission. (By referring to conditions (1) to (4) we shall in future always mean the conditions put forward on pages 10–16.) The spectral sensitivity curves and the quantum yields of these cathodes, as derived from experiments, vary within wide limits,



probably due to impurities which it is difficult to avoid when working with such chemically reactive substances. However, two general statements can be made with regard to all the Alkali metal cathodes.

Firstly, all the cathodes have a very low quantum yield of the order of 0.001% to 0.01% for visible light, i.e. between 10,000 and 100,000 photons are required to release a single photoelectron. This low absolute sensitivity is explained by the fact that the cathodes consist of metals possessing high reflection coefficients for visible light and high electrical conductivity, so that conditions (1) and (4) are not fulfilled.

The second general statement concerning the Alkali metal cathodes is that their spectral response curves show maxima which have been found by different authors at the wavelengths indicated in Table II [3]. The great spread

TABLE II

*Wavelength of Maximum Sensitivity of Alkali Metals*

	$\lambda_{max.}$
Lithium	2,800-4,050
Sodium	3,400-4,270
Potassium	4,100-4,560
Rubidium	4,600-4,810
Caesium	4,800-5,500

of the values for the maximum wavelengths shows how difficult it is to obtain reproducible maxima, but the qualitative conclusion can be drawn from the Table that the maximum is shifted from shorter to longer wavelengths in the sequence from Lithium to Caesium, i.e. from the lightest to the heaviest metal; this, of course, is in agreement with conditions (2) and (3).

#### (C) THE ALKALI HYDRIDE PHOTOCATHODE

During the early experiments with Alkali metal cathodes it was found that certain 'sensitising' processes increased the photoelectric response of the cathodes. The most

effective process [13] consisted of producing within the photocell a discharge in Hydrogen, using the Alkali metal as negative electrode and the anode as positive electrode. In the course of the discharge the cathode surface loses its metallic appearance and simultaneously the sensitivity rises to approximately ten times its original value. The effect of the discharge is the formation of a chemical compound, an Alkali Hydride (LiH, NaH, KH, &c.), which explains the changed appearance of the surface. It should be noted that if the Alkali metal is completely converted into Alkali Hydride the photoelectric sensitivity is reduced to zero. The reason for the improved photoelectric response of the 'sensitised' cathode and for the non-sensitivity of pure Alkali Hydride will be discussed later (page 31).

#### (D) THE SILVER-OXYGEN-ALKALI PHOTOCATHODE

(a) *General.* While the three types of cathodes summed up in the preceding paragraphs are now, owing to their low quantum yield, only of historical and theoretical interest, the cathodes of more complicated structure to be described in this and the following sections are of great practical importance in modern photoelectric cells. Three general statements can be made concerning all composite photocathodes:

- (1) The presence of Alkali metal is essential for response to visible light because of the overriding importance of conditions (2) and (3).
- (2) Both the quantum yield and the wavelength at which maximum sensitivity is obtained may vary within fairly wide limits for cells of the same type.
- (3) For each type of cathode the maximum sensitivity is shifted from shorter to longer wavelengths in the sequence from Lithium to Caesium, corresponding to the effect noted with plain Alkali metal cathodes (see page 20).



This last fact simplifies the description of composite photoelectric cathodes because it is only necessary to describe in detail the properties of a type of cathode containing one of the Alkali metals and we can then determine, at least approximately, how the sensitivity of the cathode would be changed by using a different Alkali metal. According to conditions (2) and (3) Caesium is always likely to yield the best results; we shall therefore confine ourselves in the case of the Silver-Oxygen-Alkali type to an account of the Silver-Oxygen-Caesium photocathode.

(b) *Manufacture of the Silver-Oxygen-Caesium cathode* [22, 33]. As the name indicates, the Silver-Oxygen-Caesium (abbreviated 'Ag-O-Cs') photocathode consists of a combination of the chemical elements Silver, Oxygen and Caesium. The first step in the manufacture of the cathode is to produce a base layer of metallic Silver within a glass bulb. This can be accomplished by either of the two following methods which are both used in actual photocell manufacture:

- (1) A solid electrode consisting of Silver sheet or, for economic reasons, of Silver-plated Nickel sheet forms the base layer of the cathode. As shown in Fig. 7 the electrode is mounted on a glass pinch in the conventional way so as to produce an electrical connection with the external lead to the cathode.
- (2) The Silver which forms the base layer is deposited on part of the inner glass wall of the bulb, as is shown in Fig. 8; in this case the electrical connection is usually provided by a Platinum strip sealed into the glass wall, this strip being welded to the end of the cathode lead-in wire. One method of depositing Silver on part of the glass wall consists of chemical precipitation. The usual process is the same as that used for silvering mir-

rors and Dewar flasks, the principle of the process being the reduction of a Silver salt solution to metallic Silver. The Silver layer thus formed adheres firmly to the glass wall and has a matt white surface owing to the irregular shape of the individual Silver particles in the layer. An alternative method of depositing Silver on the glass wall consists of evaporating a small piece of Silver

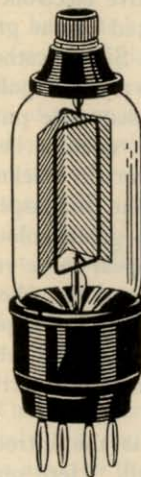


FIG. 7



FIG. 8

heated directly by a filament or from within an indirectly heated container. This method is not as simple as chemical deposition and is, as a rule, only used in the process which includes an additional evaporation of Silver at a later stage (see page 27), so that means for evaporating Silver have to be incorporated in the cell in any case.

After the bulb has been provided with the Silver base it is evacuated and degassed by baking at  $400^{\circ}\text{C}$ . (an exception is the evaporated Silver layer which is deposited



after evacuation and degassing) and is then ready for the oxidation process. Silver, being a 'noble' metal, does not react with Oxygen at high temperature; however, a very simple method for obtaining a Silver Oxide layer of accurately controlled thickness consists of exposing the Silver to a glow discharge in an Oxygen atmosphere. During a glow discharge at low Oxygen pressure (0.1 to 1 mm. Hg) between the Silver as negative electrode and the anode of the photocell as positive electrode, the progress of the oxidation can be checked by the gradual discoloration of the surface of the Silver cathode. The originally whitish surface changes to a yellow-golden colour and then goes through the colour sequence purple-blue-green; after the green stage the colours become less defined. Each colour indicates a certain thickness of the Silver Oxide layer and in practice the discharge is usually stopped between the blue and the green colour, though the degree of oxidation does not appear to be very critical in its effect on the final sensitivity of the photocathode. The blue-green colour corresponds to approximately 100 atomic layers of Silver Oxide. After the desired colour is reached, the glow discharge is interrupted and the photocell again evacuated.

The next step in the process is the introduction of metallic Caesium into the photocell. Here one is faced with the difficulty that Caesium, on exposure to air, reacts immediately with Oxygen, and therefore a rather complicated technique has to be used to produce the metallic Caesium in a side tube sealed to the bulb or within the bulb itself. According to the most usual procedure, a Nickel pellet is placed in the side tube, or mounted in the bulb, this pellet containing a mixture of a Caesium salt which is stable in air and a metal which is able to reduce this salt to metallic Caesium at high temperature. Two examples of suitable mixtures are the following:

- (1) Caesium Chloride + Calcium metal.
- (2) Caesium Chromate + Zirconium metal [7].

In both cases the ratio of metal to salt must be considerably greater than that of the equivalent atomic weights.

One essential condition which the mixture has to fulfil is that the reaction should not start below the degassing temperature of 400° C. because otherwise the Caesium developed in the pellet would be oxidised during the oxidation of the Silver base which, as mentioned above, follows the degassing process. This condition, in turn, introduces a further complication because it means that the pellet has to be heated to a temperature close to, or above, the melting-point of glass. For this reason it is necessary to use induction or eddy-current heating, by which the temperature of the metallic pellet can be raised to between 800° C. and 900° C. without undue heating of the glass.

Owing to its low evaporation temperature the Caesium formed in the pellet escapes from the latter and condenses on the colder parts of the glass wall or of the side tube. From here it is distilled on to the Silver Oxide layer and this represents the most difficult stage in manufacturing an Ag-O-Cs cathode of high sensitivity. The amount of Caesium to be distilled is very critical in both directions, i.e. too little and too much Caesium are equally detrimental. The total amount of Caesium needed is only approximately 0.25 milligrams per square centimetre of the cathode area, so that for photocells of average dimensions not more than between 1 and 10 milligrams are required. The difficulty of obtaining such small quantities with sufficient accuracy is obvious and explains why mass production of photocells of uniformly high sensitivity is not feasible. Several methods which aim at distilling the optimum amount of Caesium on to the Silver Oxide layer are described in the following:

- (1) The pellet is mounted within the bulb and contains just enough mixture, judged by experience, to produce the required quantity of Caesium metal. All the Caesium produced from the pellet is distilled on to the Silver Oxide.



- (2) The pellet is within the bulb and contains an excess amount of mixture. The bulb is provided in addition with a getter, i.e. a substance which will absorb the excess of Caesium metal.
- (3) The pellet is placed in a side tube and contains an excess amount of mixture. While the Caesium metal is slowly distilled into the cell the colour change of the cathode surface and the change of photoelectric emission are observed. The distillation is stopped and the side tube containing the unused excess Caesium is sealed off the bulb as soon as colour and photocurrent have reached an 'optimum' which has to be found by trial and error.
- (4) For experimental cells a method has been developed by which Caesium is produced from the usual mixtures but distilled into glass capillaries and not directly into the photocell. If the inside diameter of the capillaries is known the exact amount of Caesium can be calculated from the length of capillary filled with Caesium. In this way weighed quantities of Caesium can be introduced into photocells by transferring a capillary with Caesium into a side tube of the bulb and breaking it, after evacuation of bulb and side tube, by means of a magnetically controlled iron ball.

The fact that the first three methods are all used in practice and that individual photocells made by the same method still vary widely in sensitivity, prove that no one method is perfect or definitely superior to the others.

After the Caesium distillation is completed, the bulb is subjected to a baking process which again is not standardised and can vary with respect to duration and temperature. The temperature is usually between  $150^{\circ}\text{C}$ . and  $250^{\circ}\text{C}$ .; the duration depends mainly on the temperature (the higher the temperature the shorter is the required time) and on the cathode area (the larger the area the longer is

the required time). It has been found advantageous in some cases to introduce an exceedingly small amount of Oxygen into the bulb after the baking process, with subsequent re-evacuation, followed by a short second baking process. Finally, the completed photocell is sealed off the pumping system, unless it is to be gasfilled (see Chapter VI).

The description of manufacturing methods would not be complete without mentioning a more complicated process which includes the evaporation of a small amount of Silver on to the cathode either after oxidation of the Silver base or after the introduction of the Caesium. Photocells

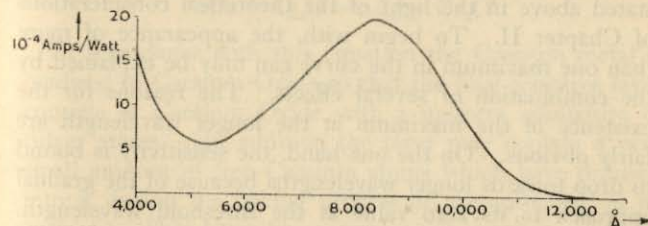


FIG. 9.—Spectral response curve of Ag-O-Cs photocathode

made by this process are of higher sensitivity, probably owing to the greater electrical conductivity of the sensitive layer (see page 30).

(c) *Properties of the Silver-Oxygen-Caesium cathode.* The main characteristics of the Ag-O-Cs photocathode can be seen from the colour response curve in Fig. 9, but it must be emphasised again that individual cathodes are not exactly identical, so that the curve shown in Fig. 9 represents only average values, not only of the quantum yield at various wavelengths but also of the wavelength at which the curve reaches a maximum.

The following facts are evident from the curve :

- (1) The sensitivity curve has at least two maxima, one in the ultra-violet (not shown in Fig. 9) and one in the near infra-red range of the spectrum.

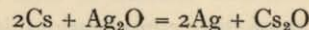


- (2) The peak sensitivity at 8,400 Å is approximately 2 milliamps. per watt, as compared with the theoretical maximum of 700 milliamps. per watt derived from curve (a) in Fig. 6. The quantum yield in the wavelength range of peak sensitivity is therefore approximately 0.3%, i.e. in the most favourable case 300 photons are required to release one electron.
- (3) The threshold wavelength  $\lambda_0$  is greater than 12,000 Å, i.e. the work function  $\phi$  is, according to equation (5), lower than 1 volt.

It will now be attempted to interpret the three facts stated above in the light of the theoretical considerations of Chapter II. To begin with, the appearance of more than one maximum in the curve can only be explained by the combination of several effects. The reasons for the existence of the maximum at the longer wavelength are fairly obvious. On the one hand, the sensitivity is bound to drop towards longer wavelengths because of the gradual approach to its zero value at the threshold wavelength. On the other hand, the drop towards shorter wavelengths is, at least partly, due to the fact that the magnitude of the quanta increases with shorter wavelengths so that the amperes per watt value must decrease, even if the quantum yield remains constant (see Fig. 6, curve (a)). But the comparatively steep drop of the curve between 8,000 and 6,000 Å, as well as the existence of the second maximum below 4,000 Å, shows that there must be another reason for the shape of the curve. A likely explanation is that the degree of light absorption varies. This may mean, in accordance with condition (1), that the maxima of the curve correspond to some extent to the maxima in the absorption curve. The light absorption of the Ag-O-Cs cathode has not been determined experimentally, so that it cannot be stated with certainty whether any further theoretical assumptions have to be made to explain the shape of the response curve.

The superiority of the Ag-O-Cs photocathode over the Alkali metal cathode is evident from its higher quantum yield and its lower work function. The higher quantum yield is, of course, partly a consequence of the reduced work function, but it is also due to the fact that conditions (1) (page 10) and (4) (page 16) are fulfilled more satisfactorily.

At this point reference must be made to the chemical structure of the Ag-O-Cs cathode. The effect of the baking process after the distillation of Caesium metal (see page 26) is to promote a chemical reaction which is expressed by the equation



In accordance with this equation the Caesium metal is oxidised to Caesium Oxide so that the final sensitive layer consists of Caesium Oxide with a uniform admixture of Silver atoms. (In addition the layer may contain a very small amount of free Caesium atoms which have diffused into it during the baking process or are adsorbed on its surface.) This layer has a very much smaller reflection coefficient than pure Caesium metal and is therefore superior to the pure metal with regard to condition (1). Moreover it has, obviously, a higher specific resistance than a pure metal. Here it must be remembered that condition (4) demands a specific resistance intermediate between that of a metallic conductor and that of an insulator. The three following experimental facts suggest that the Ag-O-Cs layer represents such a layer of intermediate specific resistance.

(1) As it is probable that the photoelectrons originate from the Caesium atoms contained in the Caesium Oxide and not from the Silver atoms, one might expect greater sensitivity from pure Caesium Oxide than from the mixture of Caesium Oxide and Silver. However, experiments have shown that the sensitivity in the absence of Silver is much smaller, i.e. the highly conducting Silver reduces the



specific resistance to a lower, apparently more favourable, value.

(2) If the amount of Silver in the layer is further increased, as is done in the more complicated manufacturing process described on page 27, greater sensitivity is achieved. This is most probably due to a further reduction of the specific resistance since there is no other explanation for the effect of the additional Silver.

(3) Cathodes in which the Silver has been replaced by other metals are of lower sensitivity than the Ag-O-Cs cathode. It seems reasonable to explain this by the fact that the conductivity of Silver is greater than that of any other metal.

Summarising these three considerations, it would appear that by mixing Caesium Oxide with particles of high electrical conductivity layers of optimum specific resistance are produced.

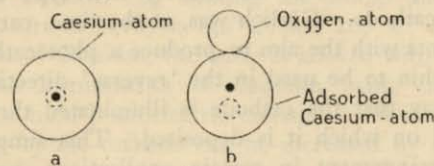
The third fact concerning the Ag-O-Cs photocathode, as mentioned on page 28, is the low value of the work function as derived from the measurement of the threshold wavelength. Referring to Table I (page 14), there is an evident discrepancy between the value of  $\phi = 1.4$  volts, given in the Table for Caesium, and the value  $\phi \approx 1$  volt found for the Ag-O-Cs cathode. But we must remember that the values in Table I refer to chemical elements, while in the case of the Ag-O-Cs cathode we are considering a complicated chemical structure.

According to a generally accepted theory, the surface layer of the Ag-O-Cs cathode consists of Caesium Oxide molecules to which individual atoms of metallic Caesium are attached by adsorption forces. The existence of such free, as distinct from chemically bound, Caesium atoms can be proved experimentally as follows:

If the total amount of Caesium present in the layer were bound chemically by Oxygen, exposure of the cathode to Oxygen should not have any effect on its photoelectric sensitivity. In reality, however, if Oxygen is gradually

introduced into the completed photocell the sensitivity decreases and finally disappears completely. Referring back to the Alkali Hydride photocathode (page 21), the superiority of this cathode over the plain Alkali metal cathode has also been explained by the existence of an adsorbed layer of free Alkali metal atoms, the Alkali Hydride molecules corresponding to the Caesium Oxide molecules in the case of the Ag-O-Cs cathode. The experimental proof is on similar lines, i.e. pure Alkali Hydride is not photoelectrically sensitive and a slight excess of metallic Alkali is essential.

It is now our task to explain why the adsorption of a mono-atomic layer of metallic Caesium on the surface



of the Ag-O-Cs cathode should reduce the work function of that surface. We can assume that in neutral Caesium atoms, like those which occur if the metal is present in bulk, as for instance in the simple Alkali metal photocathode, the centres of positive and negative charge coincide. This is shown diagrammatically in Fig. 10 (a), in which positive charge is indicated by a dot and negative charge by a dotted ring. Fig. 10 (b) represents a Caesium atom which is bound by adsorption to a Caesium Oxide molecule. In this case the centres of positive and negative charge no longer coincide and the atom is 'polarised', with the result that less energy is required to separate one electron completely from the atom, i.e. to ionise it. As we have seen on page 15, reduced ionisation energy corresponds to reduced work function, therefore both conditions (2) and (3) are more satisfactorily fulfilled for adsorbed Caesium than for Caesium metal in bulk.



The above description of the properties of adsorbed mono-atomic layers of Alkali metal and their effects on the electron emission of surface layers is based on a simplified representation of very complex phenomena. An exhaustive discussion of the subject can, however, be found in the literature [4].

#### (E) THE ANTIMONY-ALKALI PHOTOCATHODE

(a) *General.* Since their development between 1928 and 1930 photocathodes of the Silver-Oxygen-Alkali type were almost exclusively used for all applications which required sensitivity to visible light, until in 1936 Görlich [16-20] discovered an entirely new type of photo-sensitive cathode. Görlich was, at the time, carrying out experiments with the aim to produce a photocathode sufficiently thin to be used in the 'reverse' direction, i.e. in such a way that the cathode is illuminated through the glass wall on which it is deposited. This simplifies the optical arrangement in certain applications, particularly for television transmission, because the anode and, in tubes of more complicated structure, any additional electrodes can be mounted in any desired position in front of the cathode without interfering with the light beam.

The Ag-O-Cs cathode seemed to be unsuitable for this purpose because the light entering from the back of the cathode is partly reflected or absorbed by the Silver base layer. Therefore Görlich tried to produce alloys of Alkali metals with other metals which do not require an additional metallic base layer. His experiments showed that the Alkali metals form stable alloys of useful photoelectric sensitivity with the metals Antimony, Bismuth, Thallium and Lead [16]. Among these metals Antimony appeared to be the most promising and, as in the case of the cathodes previously discussed, Caesium proved to be the most suitable Alkali metal. In the following we shall therefore confine ourselves chiefly to the Antimony-Caesium alloy.

(b) *Manufacture of the Antimony-Caesium cathode.* The

manufacture of the alloy cathode can be dealt with in a few lines because in many respects it is similar to that of the Ag-O-Cs cathode. The alloy layer is deposited either on the glass wall or on a solid metallic electrode. (In this case it cannot, of course, be used for its original purpose, i.e. for illumination from the back of the cathode; but for most applications illumination from the front of the cathode is preferable.) The first step of the process consists in evaporating a small piece of Antimony by one of the methods described for the evaporation of Silver, on page 23. Next, metallic Caesium is introduced into the photocell, again in the same way as in the case of the Ag-O-Cs cathode. By heating the whole photocell to a temperature of between 150° C. and 200° C. during the distillation of Caesium, the latter is alloyed with the Antimony, the introduction of Caesium being interrupted when maximum photoelectric emission is obtained. The sensitivity of the cathode can be increased by superficial oxidation (see page 41).

(c) *Properties of the Antimony-Caesium cathode.* The spectral response curve of the alloy cathode is shown in Fig. 11. The sensitivity of this cathode is so much greater than that of the Ag-O-Cs cathode that the scale chosen

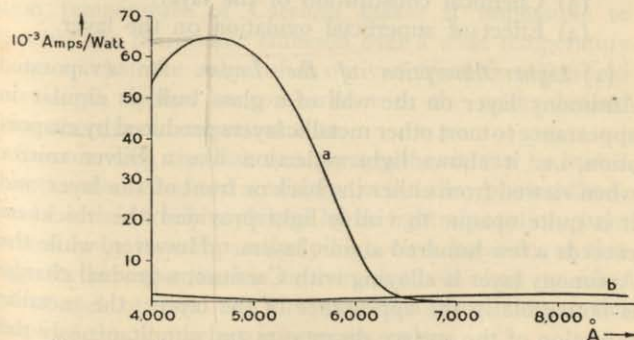


FIG. 11.—Spectral response curves of Sb-Cs (a) and Ag-O-Cs (b) photocathodes



for the ordinate has been reduced by the factor ten as compared with Fig. 9; for reference, the response curve of the Ag-O-Cs cathode is redrawn in Fig. 11. From the curve of the alloy cathode it is evident that the peak sensitivity is obtained for wavelengths near the blue end of the visible spectrum and that this peak corresponds to a maximum quantum yield of 20%, this value being again derived from curve (a) in Fig. 6. It can also be seen from Fig. 11 that the sensitivity of the alloy cathode for red light is smaller than that of the Ag-O-Cs cathode.

The Antimony-Caesium alloy consists of only two components, as compared with the three chemical elements contained in the Ag-O-Cs cathode, and this simplicity of its constitution makes it suitable for a more quantitative examination of its chemical structure and physical properties. In order to find out to what extent the outstanding photoelectric sensitivity of the alloy can be explained by the considerations which led to the four conditions for photoelectric emission (page 10), the writer [38] investigated the Antimony-Caesium alloy with respect to the following four characteristics:

- (1) Light absorption of the alloy layer.
- (2) Specific resistance of the layer.
- (3) Chemical constitution of the layer.
- (4) Effect of superficial oxidation on the layer.

(1) *Light Absorption of the Layer.* An evaporated Antimony layer on the wall of a glass bulb is similar in appearance to most other metallic layers produced by evaporation, i.e. it shows light reflection like a Silver mirror when viewed from either the back or front of the layer and it is quite opaque to visible light provided the thickness exceeds a few hundred atomic layers. However, while the Antimony layer is alloying with Caesium, a gradual change is noticeable in the appearance of the layer; the metallic reflection of the surface disappears and simultaneously the layer becomes partially transparent, particularly for light

of wavelengths above 5,500 Å. The alloy layer of highest photoelectric sensitivity has a surface of greyish colour with reflected light and a beautiful ruby colour with transmitted light.

The absorption curve of the alloy layer has not been measured accurately, but it has been established that it is in qualitative agreement with the photoelectric response curve (Fig. 11), i.e. the layer is not photoelectrically sensitive to light in the wavelength range which is not strongly absorbed. This correspondence of light absorption curve and photoelectric response curve is in accordance with condition (1).

There is, however, an additional reason for the absence of sensitivity to red light, i.e. the work function of the layer is higher (and consequently the threshold wavelength lower) than that of the Ag-O-Cs layer. Qualitative information concerning the relative  $\phi$  values of the Ag-O-Cs and the alloy layers has been obtained from measurements of the thermionic emission of both layers. It has been found that the thermionic emission at room temperature is at least 1,000 times greater in the case of the Ag-O-Cs layer than in the case of the alloy layer; this means that the work function of the alloy layer must be considerably greater than that of the Ag-O-Cs layer. The low evaporation temperature of Caesium makes it impossible to measure the thermionic emission over a wide temperature range so that the value of  $\phi$  derived from the threshold wavelength cannot be compared with the value derived from thermionic measurements.

Summarising the last two paragraphs, it can be stated that the absence of red sensitivity in the alloy photocathode can be satisfactorily explained by its light-absorption curve as well as by its comparatively high work function, so that only further quantitative experiments will show to what extent each of these two characteristics contributes to the shape of the photoelectric response curve.

- (2) *Specific Resistance of the Antimony-Caesium Cathode.*



Measurements made with the photoelectrically sensitive alloy layer showed that the specific resistance of the layer is approximately one million times greater than that of pure Antimony metal and ten million times greater than that of pure Caesium metal. It is a well-known fact that the resistance of an alloy is greater than that of the individual metals contained in it, but as a rule the resistance of the alloy does not exceed that of its component of highest resistance by a factor greater than ten. Therefore the increase of specific resistance by the factor  $10^6$  in the case of the Antimony-Caesium alloy is a most unexpected phenomenon which can only be explained by the chemical structure of the alloy (see the following section).

The high specific resistance of the alloy is significant in relation to its photoelectric emission. Referring to condition (4) for photoelectric emission (page 16) one would not expect a high quantum yield from a cathode consisting of an alloy, i.e. from a cathode formed of metals only, but this contradiction is removed if the alloy does not show metallic conductivity. Actually one can conclude from the high quantum yield of the alloy layer that the value of its specific resistance must be close to the optimum value required by condition (4).

(3) *Chemical Constitution of the Antimony-Caesium Cathode.* In the description of the manufacturing process it was mentioned that the distillation of Caesium on to the Antimony layer is stopped when the maximum photoelectric sensitivity is reached. The fact that the sensitivity drops if the distillation of Caesium is continued points to the probability that maximum photoelectric sensitivity corresponds to a certain ratio of Antimony to Caesium in the alloy.

This ratio has been determined experimentally as follows (for further details see the original paper [38]): A weighed amount of Antimony is first evaporated on to the wall of a glass bulb in the usual manner and then a weighed amount of Caesium is partially distilled into the

bulb from a side tube so as to alloy with the evaporated Antimony layer. The process is stopped as soon as the photoelectric sensitivity reaches its maximum; the unused fraction of the original amount of Caesium is then weighed and the amount of Caesium contained in the alloy layer is calculated as the difference between the weight of the original amount of Caesium in the side tube and the unused amount.

Repeated quantitative experiments of this type proved that the photoelectrically sensitive alloy of highest quantum yield contains the metals Antimony and Caesium in the ratio 1:3, corresponding to a chemical formula  $\text{SbCs}_3$ . We cannot go into details concerning the chemical aspects of this experimental result, but a few remarks may show the significance of the above formula both generally and particularly with regard to the photoelectric sensitivity of the alloy cathode.

Among the combinations of metals with each other one can distinguish between alloys and 'intermetallic compounds', although a strict dividing-line between the two types does not exist. According to a simple definition an alloy comprises metals which can be mixed with each other in any ratio within a wide range to form a homogeneous substance of metallic appearance, the properties of which vary continuously with the changing ratio. An intermetallic compound, on the other hand, consists of metals in a fixed ratio, often in accordance with the valency of the constituents, and its properties change rather abruptly if the ratio does not correspond to the stoichiometric formula.

From these definitions of alloy and intermetallic compound it can be seen that the photoelectric Antimony-Caesium layer represents a typical intermetallic compound, of the formula  $\text{SbCs}_3$ . The valencies of Antimony and Caesium are 3 (in compounds with electro-positive elements) and 1 respectively, so that the formula  $\text{SbCs}_3$  is to be expected. Moreover, the physical properties of



the layer are more in agreement with the conception of a chemical compound than with the conception of an alloy. The three most striking characteristics of the  $\text{SbCs}_3$  layer are, firstly, its non-metallic appearance, secondly, its non-metallic specific resistance, and thirdly, its high photoelectric sensitivity.

The realisation that the Antimony-Caesium (from now on abbreviated 'Sb-Cs') photocathode consists of a chemical compound rather than of an alloy helps to explain its high photoelectric sensitivity as compared, not only with the pure Caesium cathode, but also with the Ag-O-Cs cathode. On page 30 the relatively high sensitivity of the Ag-O-Cs cathode was attributed to the fact that it consists of Caesium Oxide (and interspersed Silver atoms) with a mono-atomic surface layer of metallic Caesium. In a similar way one can consider the Sb-Cs cathode as consisting of  $\text{SbCs}_3$  'compound' with an adsorbed surface layer of free Caesium atoms. (The experiments leading to the formula  $\text{SbCs}_3$  are, of course, not sufficiently accurate to reveal, by a deviation from the ratio 3 : 1 of the elements, the exceedingly small amount of free Caesium.)

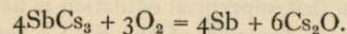
If the Sb-Cs cathode and the Ag-O-Cs cathode are, as suggested in the previous paragraph, of a fundamentally similar chemical structure, the question arises why the quantum yield of the Sb-Cs cathode is so much greater than that of the Ag-O-Cs cathode. Two answers are possible to this question, but they are—at least for the present—only of a hypothetical nature.

Firstly, the Sb-Cs cathode consists entirely of what may be called 'photoelectric centres', while the Caesium Oxide in the Ag-O-Cs cathode is 'diluted' by non-photoelectric Silver atoms which absorb or reflect part of the incident light. These Silver atoms are, however, essential to reduce the internal resistance of the Ag-O-Cs layer, this being evident from the fact that a layer consisting only of Caesium Oxide with adsorbed Caesium is much less sensitive than the same layer with the addition of Silver.

A second reason for the superiority of the Sb-Cs cathode may be the fact that its specific resistance is nearer to the optimum value than that of the Ag-O-Cs cathode.

(4) *Effect of Superficial Oxidation on the Antimony-Caesium Cathode.* The effects of Oxygen on the Sb-Cs cathode have been investigated because they provide valuable clues regarding the mechanism of photoelectric emission from composite layers of the type of the Sb-Cs layer. Before describing the experimental results it may be useful to consider what effects exposure to Oxygen is likely to have on the Sb-Cs layer if we assume that the characteristics of the layer are determined by the factors discussed in the preceding paragraphs.

Owing to its great affinity for Caesium, Oxygen will react with the Sb-Cs layer (in which the Caesium is bound only comparatively loosely to the Antimony) according to the equation



This means that two new chemical entities are introduced into the hitherto homogeneous layer, viz. free Antimony metal and Caesium Oxide. This change of chemical composition is likely to affect the properties of the layer as follows:

- (1) The creation of free metal (Antimony) will reduce the specific resistance of the layer.
- (2) The 'dilution' of the photoelectric compound  $\text{SbCs}_3$  with non-photoelectric free Antimony metal will reduce the quantum yield in analogy to the 'diluting' effect of the Silver in the case of the Ag-O-Cs cathode (see page 38).
- (3) The creation of Caesium Oxide near the surface of the cathode will produce a surface layer consisting, at least partially, of free Caesium atoms which are adsorbed on Caesium Oxide instead of on Antimony as was the case before the introduction of Oxygen. Such a change will reduce the



work function of the layer for the following reason :

It was previously (page 30) mentioned that the low work function of Caesium when adsorbed by the Oxygen of the Caesium Oxide is due to the polarisation of the Caesium atoms. Now it is reasonable to assume that the most electronegative atoms will exert the most pronounced polarising effect on Caesium atoms ; therefore, if one compares Caesium atoms adsorbed on Antimony (as in the case of the Sb-Cs cathode) with Caesium atoms adsorbed on the much more electronegative Oxygen (as in the case of the superficially oxidised Sb-Cs cathode and also in the case of the Ag-O-Cs cathode), a lower work function and consequently a longer threshold wavelength are to be expected in the case of adsorption on Oxygen. This means that superficial oxidation is likely to reduce the work function of the Sb-Cs cathode and so increase its photoelectric sensitivity, particularly to light of longer wavelengths.

Summarising the above considerations, it is to be expected that the photoelectric sensitivity of the Sb-Cs cathode is reduced as a result of the formation of free Antimony metal and that it is increased as a result of the formation of Caesium Oxide, but it can only be decided by experiments which of these two effects is predominant, i.e. whether the sensitivity of the cathode is on balance increased or reduced by oxidation. In the following paragraphs we shall discuss briefly the results of the experiments with oxidised  $\text{SbCs}_3$  cathodes.

In accordance with expectation, the specific resistance of the Sb-Cs layer is reduced by superficial oxidation whilst the photoelectric sensitivity increases to a maximum value and then drops gradually to zero if the introduction of Oxygen is continued. It is not surprising that an excess of Oxygen is detrimental to the photoelectric sensitivity

because the excess will not only oxidise the essential monoatomic surface layer of free Caesium but will also decompose completely, according to the above-quoted chemical equation, the photoelectric centres consisting of  $\text{SbCs}_3$ .

To gain a closer insight into the effect of oxidation on the electron emission, the change of sensitivity for light of two different wavelength ranges was examined by introducing Oxygen in very small quantities at a time and measuring the photoelectric sensitivity after each introduction. For these experiments an incandescent lamp was used in connection with a red filter (transmission approximately above  $5,700 \text{ \AA}$ ) or a blue-green filter (transmission approximately below  $5,700 \text{ \AA}$ ). The results of a typical series of measurements are shown in Table III.

TABLE III

Steps of Oxidation	% of Maximum Sensitivity to	
	Red ( $\lambda > 5,700 \text{ \AA}$ )	Blue-Green ( $\lambda < 5,700 \text{ \AA}$ )
0	3.5	59
1	4.0	64
2	5.0	70
3	8.5	75
4	22	94
5	55	100
6	100	82
7	93	62
8	86	46
9	41	25
10	38	16

From this Table it is evident that the sensitivity for long wavelengths continues to increase after the maximum for short wavelengths has been passed. This finding is in agreement with the assumption that any increase of sensitivity is due to a lowering of the work function, because the electrons which are released by red light have low initial velocities and are therefore in greater 'need' of a low work function than the comparatively fast electrons



released by light of shorter wavelengths. In other words, the point where the beneficial effect of the Oxygen on the work function is balanced by the detrimental effect of the Oxygen on the photoelectric centres is reached at a later stage of the oxidation process for light of longer wavelengths than for light of shorter wavelengths.

(d) *Summary.* The properties of the Antimony-Caesium cathode have been described in detail because they provide a great amount of information concerning the mechanism of photoelectric emission. At this point it must be emphasised that most of the conclusions drawn from the experimental facts as well as the four conditions for photoelectric emission postulated on page 10, can only claim the status of working hypotheses, but it may be useful to show how these working hypotheses are able to explain the exceptionally high quantum yield of the Antimony-Caesium cathode by comparing in a concise form the characteristics of the cathode with these four conditions for photoelectric emission.

(1) *High degree of light absorption.* The Sb-Cs layer does not show metallic reflection; it absorbs light only up to approximately 6,000 Å and is therefore of very low sensitivity to red light.

(2) *Low ionisation energy.* The Sb-Cs layer contains Caesium, which has the lowest ionisation energy of all the chemical elements.

(3) *Low work function.* The surface layer of the Sb-Cs cathode consists of Caesium adsorbed by Antimony, which has a lower work function than Caesium in bulk. The work function of Caesium adsorbed by Oxygen is even lower than that of Caesium adsorbed by Antimony, hence both the Ag-O-Cs cathode and the superficially oxidised Sb-Cs cathodes are more sensitive to red light than the homogeneous Sb-Cs cathode.

(4) *Specific resistance of semiconductor.* The resistance of the Sb-Cs layer is one million times greater than that of metals.

#### (F) VARIOUS ALLOY PHOTOCATHODES

As has been mentioned previously, the Antimony-Caesium photocathode is of much greater photoelectric sensitivity than any of the other alloy cathodes, but in order to make the survey complete, a very short account will be given of these other cathodes. Alloys of Antimony with Alkali metals other than Caesium [16, 28, 38] and alloys of Arsenic [15], Bismuth [15, 16, 28, 38], Thallium [16], Lead [16] and Gold [39] with Caesium and other Alkali metals have been produced and investigated. With regard to their chemical structure, they appear to be similar to the Antimony-Caesium alloy, i.e. they form intermetallic compounds of stoichiometric formulae in accordance with the valencies of their constituents. As regards the Arsenic-Caesium alloy it must be added that it has not been studied in sufficient detail to ascertain whether or not it is of lower sensitivity than the Antimony-Caesium alloy; this is due to the fact that experiments in vacuum with Arsenic are made difficult by its very low sublimation temperature.

The superiority with respect to photoelectric emission of the Antimony-Caesium intermetallic compound as compared with compounds consisting of other metals can be explained qualitatively as follows. The superiority of Caesium over all other Alkali metals has already been discussed and does not require any further comment; the superiority of Antimony over other metals forming intermetallic compounds with Caesium can be attributed to the fact that owing to its electronegative character in comparison with other metals it has the strongest polarising effect on Caesium and therefore tends to aid the release of photoelectrons.

It may be objected that all non-metallic elements which form compounds with Caesium (for instance Oxygen, the Halogens, &c.) should, owing to their more electronegative character, produce, when combined with Caesium, even better photoelectric emitters than Antimony, but in their



case low light absorption and high specific resistance make high photoelectric sensitivity impossible. In other words, the outstanding properties of the Antimony compounds seem to be due to the place of Antimony among the chemical elements on the border-line between metals and non-metals.

The last type of photocathode to be described has only been developed in recent years and is distinguished by the fact that it contains four chemical elements, viz. Bismuth, Silver, Oxygen and Caesium [9, 10]. The colour response

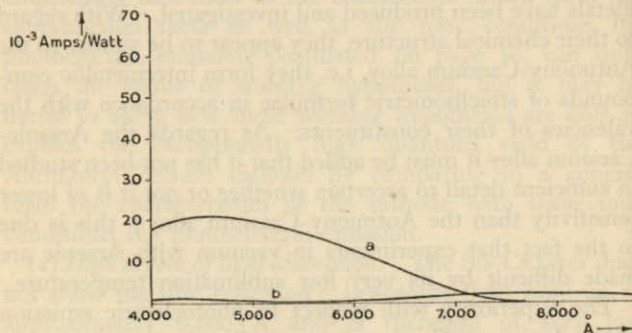


FIG. 12.—Spectral Response Curves of Bi-O-Ag-Cs (a) and Ag-O-Cs (b) photocathodes

curve of this cathode is shown in Fig. 12, from which it can be seen that the maximum quantum yield is second only to that of the  $\text{SbCs}_3$  cathode. The most significant characteristic of this 'Bi-O-Ag-Cs' cathode is its comparatively uniform sensitivity throughout the visible spectrum.

The process by which the Bi-O-Ag-Cs cathode is manufactured has, at the date of writing, only been disclosed in Patents. The structure of the cathode is obviously more complicated than that of cathodes containing three or less chemical elements (like the Ag-O-Cs and Sb-Cs cathodes), and attempts at a theoretical interpretation of its properties have not yet succeeded.

## CHAPTER IV

### MATCHING OF LIGHT SOURCES AND PHOTOCATHODES

IN most applications of photoelectric cells it is desirable to obtain the largest possible photoelectric current for a given amount of light. Owing to the fact that all light sources of practical importance emit varying amounts of light in different wavelength ranges, it is obviously essential to use for each light source a photocathode which has maximum response in the wavelength range where the light source has maximum emission. Whilst the colour response of photocathodes has been discussed in the preceding Chapter, it is the purpose of the present Chapter, firstly, to give a survey of the emission spectra of the most important light sources and, secondly, to show briefly how each light source can be matched with the most suitable photocathode by combining the information obtained from the response curves of photocathodes with that obtained from the emission curves of light sources.

#### (A) LIGHT SOURCES

For the discussion of light sources it is useful to make a distinction between thermal light sources and all other types. The first group includes the most important practical light sources, viz. incandescent lamps and sunlight. In the second group we shall confine ourselves to some points concerning gas discharge lamps and fluorescent materials which are of interest in connection with photoelectric cells.

(a) *Thermal light sources.* The amount of energy radiated at a certain wavelength by a hot solid body is a function solely of the temperature and is determined by Planck's law of radiation as expressed by the following equation (this equation is only strictly valid for 'ideal black bodies', but for our present considerations we shall assume



that the equation applies to the thermal light sources of practical importance):

$$E_{\lambda} = \frac{c_1}{\lambda^5} \times \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}$$

In this equation  $E_{\lambda}$  is the energy radiated at wavelength  $\lambda$ ,  $c_1$  and  $c_2$  are constants and  $T$  is the absolute temperature. Spectral emission curves, as derived from Planck's equation,

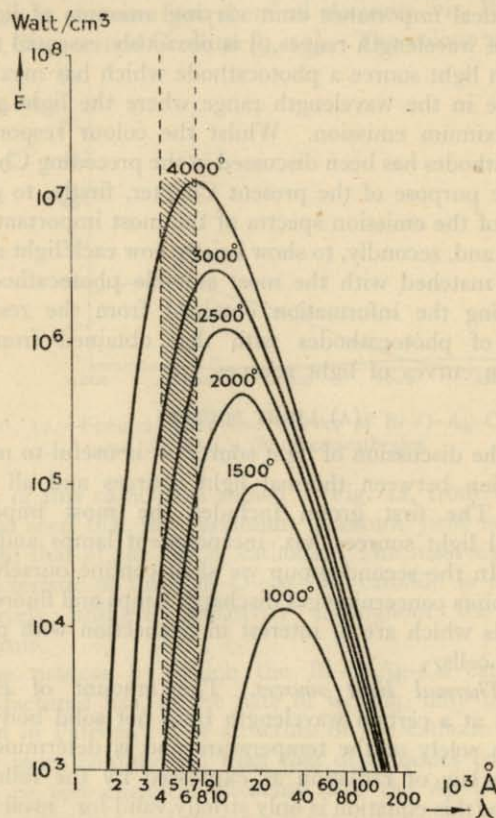


FIG. 13

for temperatures between 1,000° K. and 4,000° K. are shown in Fig. 13, in which the emitted energy, expressed in watts/cm.<sup>2</sup>, is plotted on a logarithmic scale against the wavelength  $\lambda$  for a wavelength range extending from the ultra-violet (2,000 Å) to the infra-red (200,000 Å). The visible wavelength range (4,000 Å to 7,600 Å) is indicated by shading.

From the curves in Fig. 13 it can be seen that up to 1,500° K. practically the whole radiation is emitted in the infra-red wavelength range and that only above 4,000° K. the wavelength of maximum emission is within the visible range. The relative amounts of emission in different wavelength ranges are illustrated more clearly still by Table IV [24], which shows for various temperatures the

TABLE IV  
Energy (in Percentage of Total Energy) emitted at various Temperatures

Temperature (° K.)	Wavelength range		
	$\lambda < 4,000 \text{ Å}$	$4,000 \text{ Å} < \lambda < 7,600 \text{ Å}$	$\lambda > 7,600 \text{ Å}$
1,000 (dull red heat)	—	0.001	100
2,000 (red-yellow)	0.0017	1.43	98.6
2,400	0.02	4.28	95.7
2,800 } (tungsten lamp)	0.11	8.78	91.1
3,000 }	0.22	11.51	88.3
5,000	6.8	37.8	55.5
6,000 (sun)	14.2	43.4	42.5
10,000	48.3	35.7	16.0

percentages of the total radiated energy that are emitted within three separate wavelength ranges, viz. the ultra-violet range ( $\lambda < 4,000 \text{ Å}$ ), the visible range and the infra-red range ( $\lambda > 7,600 \text{ Å}$ ).

From Table IV the following facts are evident:

- (1) The radiation of a hot body becomes visible to the human eye at a temperature (1,000° K.) at which only one-thousandth of one per cent of the total



radiated energy is emitted within the visible wavelength range.

- (2) Incandescent lamps which have a temperature varying, as a rule, between  $2,400^{\circ}\text{K.}$  and  $3,000^{\circ}\text{K.}$ , emit only up to approximately 10% of their total radiation in the visible range while practically all the remaining radiation is emitted in the infra-red range.
- (3) At the temperature of the sun (approximately  $6,000^{\circ}\text{K.}$ ) a greater percentage of the total radiation is emitted in the visible range than at any lower or higher temperature. It may be mentioned in passing that this fact shows how wonderfully well the human eye is adapted to the only natural light source which was available before the development of artificial sources. Even at the temperature of the sun the part of the invisible radiation emitted in the infra-red range is three times larger than that emitted in the ultra-violet range; this indicates that all thermal sources are of very low efficiency as emitters of ultra-violet radiation.

(b) *Other light sources.* All non-thermal light sources differ from the thermal sources in that their emission spectra are not represented by curves which can be calculated from a comparatively simple equation, corresponding to Planck's formula for the radiation of hot bodies.

In the case of gas discharge tubes the emission spectrum consists of distinct lines or bands which are sometimes superimposed on a continuous spectrum. It is outside the scope of this monograph to discuss in detail the different types of gas discharge tubes, but it may be useful to mention one phenomenon which is of importance if a suitable photocathode has to be selected for use in connection with a particular discharge tube. This is the fact that the colour of a discharge, as it appears to the human eye, is often misleading as a guide to the real spectral distribution

of the emitted light. A typical example is the Neon discharge which, despite its red appearance, emits an appreciable amount of radiation in the green wavelength range.

The emission spectra of fluorescent screens consist in most cases of broad bands which are determined not only by the chemical constitution of the particular screen but also by the type of excitation, i.e. the same screen frequently fluoresces in a different colour according to whether it is excited by ultra-violet radiation or by electrons. As in the case of discharge tubes the spectral distribution of the screen does not always coincide with the colour as it appears to the human eye and, in particular, screens with white fluorescence emit a greater amount of blue light than one would expect from visual observation.

#### (B) MEASUREMENT OF THE EFFICIENCY OF PHOTOCATHODES

Owing to the facts that different light sources vary to such an extent in their emission spectra and that, as has already been mentioned, even photocathodes of the same type vary appreciably in their colour response curves, the ratio of the sensitivities of any two photocathodes is likely to be different for each light source. The only accurate method of comparing the sensitivities of photocathodes consists in measuring and comparing their spectral response curves, but this method is too slow and costly for practical purposes.

In order to simplify the comparison of photocathodes for practical use it has been agreed internationally to measure the sensitivity of photoelectric cells to the radiation of a thermal light source of fixed temperature so that the energy distribution of the emission spectrum can be determined from Planck's formula. The light source that has been chosen as a standard is an incandescent lamp having a colour temperature of  $2,848^{\circ}\text{K.}$

Having thus standardised the 'quality' of the light incident on the photocathode it remains now to standardise



the quantity of the light. This quantity is determined by the luminous flux, expressed in units of lumens, to which the cathode is exposed. According to definition, the number of lumens ( $L$ ) incident on a photocathode is given by the equation

$$L = \frac{C \times A}{d^2}.$$

In this equation  $C$  is the intensity of the light source expressed in candle-power,  $A$  is the area of the photocathode in square centimetres and  $d$  is the distance of the source from the photocathode in centimetres.

Summarising the last two paragraphs, it can be stated that in practice the sensitivity of a photocathode is determined by measuring how many microamperes of photoelectric current are produced by one lumen of light radiated by an incandescent lamp having a colour temperature of  $2,848^\circ \text{K}$ . This value is usually abbreviated  $\mu\text{A/L}$ .

The significance of using a thermal light source of  $2,848^\circ \text{K}$ . as a standard can be appreciated by referring to Fig. 13 from which it is evident firstly, that this light source has a maximum emission in the near infra-red wavelength range (at approximately  $10,000 \text{ \AA}$ ); secondly, that by far the greatest part of the total radiated energy is emitted in the infra-red range and, thirdly, that in the visible range the emitted energy at the violet end of the spectrum is less than one-tenth of that emitted at the longest visible wavelength.

Bearing these considerations in mind, it is obvious that the  $\mu\text{A/L}$  value of a photocathode gives a distorted conception of the real sensitivity, as expressed in quantum yield, because a cathode sensitive to infra-red radiation will have a much greater  $\mu\text{A/L}$  value than a cathode of identical quantum yield which is sensitive to blue light. As regards the cathodes described in Chapter III, this means (if we confine ourselves to the three most important types represented in Figs. 9, 11 and 12) that the Ag-O-Cs cathode with its great response to infra-red radiation will

have  $\mu\text{A/L}$  values of the same order as the Sb-Cs and the Bi-O-Ag-Cs cathodes, despite the very much larger quantum yields of the two last-named types.

The conditions are illustrated by the curves in Fig. 14 which are derived from the curves in Figs. 9, 11 and 12 in the following way: In Figs. 9, 11 and 12 the photo-

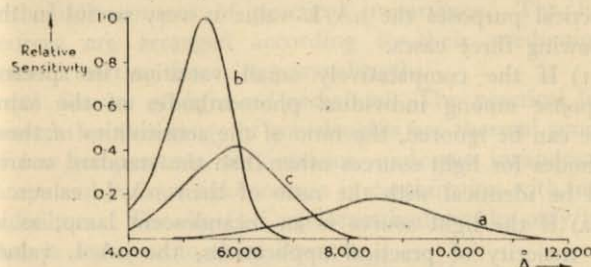


FIG. 14.—Relative sensitivities to tungsten lamp of Ag-O-Cs (a), Sb-Cs (b) and Bi-O-Ag-Cs (c) photocathodes

electric currents emitted at every wavelength are shown as calculated for an ideal light source radiating equal amounts of energy at every wavelength. In Fig. 14 the corresponding currents are plotted for the standard light source which radiates, in accordance with Planck's formula, greater amounts of energy at long than at short wavelengths. The ratio of the total areas covered by any two of the curves of Fig. 14 represents the ratio of the sensitivities of the respective photocathodes expressed in  $\mu\text{A/L}$ .

The  $\mu\text{A/L}$  values obtained with individual photocathodes of the same type vary appreciably in photoelectric cells manufactured by production methods, but the following list of minimum and maximum figures gives an indication of the values that can be expected.

Type of cathode	$\mu\text{A/L}$
Ag-O-Cs	10 to 60
Sb-Cs	30 to 100
Bi-O-Ag-Cs	10 to 60
Ag-O-Rb	up to 30
All other types	less than 10



It has been shown in the preceding paragraphs that the  $\mu\text{A/L}$  value of a photocathode gives only a limited indication of its actual sensitivity, but it must be emphasised that there does not exist any simple method of expressing the sensitivity on the basis of only one measurement, which could furnish a greater amount of information. For practical purposes the  $\mu\text{A/L}$  value is very useful in the following three cases.

(1) If the comparatively small variation in spectral response among individual photocathodes of the same type can be ignored, the ratio of the sensitivities of these cathodes for light sources other than the standard source will be identical with the ratio of their  $\mu\text{A/L}$  values.

(2) If the light source is an incandescent lamp, as in the majority of practical applications, the  $\mu\text{A/L}$  values will give the required information even for different types of cathodes, provided the colour temperature of the lamp is not too much above or below the standard of  $2,848^\circ\text{K}$ .

(3) The  $\mu\text{A/L}$  values of photocathodes of different types will give some idea regarding their relative sensitivities for *all* thermal light sources, irrespective of temperature, provided the general shape of the response curves of the cathodes is known. From the curves of Fig. 13 it is evident that if, for example, an Ag-O-Cs cathode and an Sb-Cs cathode have identical  $\mu\text{A/L}$  values, the red-sensitive Ag-O-Cs cathode will be more sensitive than the blue-sensitive Sb-Cs cathode to a thermal source of a temperature below  $2,848^\circ\text{K}$ ., and the reverse will be true for a source of a temperature above  $2,848^\circ\text{K}$ .

#### (C) EXAMPLES OF SUITABLE PHOTOCATHODES FOR SOME LIGHT SOURCES

Whereas the  $\mu\text{A/L}$  values of different types of photocathodes are useful in connection with thermal light sources they give very little indication of the relative sensitivities in the case of all other light sources. The choice of the most suitable photocathode for use with

discharge lamps and fluorescent screens has to be made either by comparing the response curves of different types of photocathodes with the emission curves of the light sources, or by the method of trial and error.

In the following, a summary will be given of the photocathodes which have been found most suitable in connection with light sources of practical importance. The light sources are arranged according to their predominant colour, starting from long wavelengths.

(1) *Sources of infra-red radiation.* The practical light sources for this range of wavelengths are thermal sources of low temperature, for instance, underrun incandescent lamps and various light sources in combination with infra-red filters. The Ag-O-Cs photocathode is the only type that is sensitive to these sources.

(2) *Incandescent lamps.* The Sb-Cs cathode is the most sensitive type, as can be seen from the  $\mu\text{A/L}$  values quoted above. Although the Ag-O-Cs cathode is of two to five times lower sensitivity than the Sb-Cs cathode, it has the advantage, as will be discussed in more detail later, of being more stable if exposed to very strong illumination and if used in gasfilled photocells.

(3) *Carbon-arc.* The carbon-arc, being a thermal source of considerably higher temperature than the incandescent lamp, emits a greater proportion of short-wavelength radiation than the latter. Hence the Sb-Cs cathode is most suitable (with the limitation regarding strong illumination and gasfilled cells mentioned under (2)).

(4) *Sunlight.* The sun is a thermal source of approximately  $6,000^\circ\text{K}$ .; therefore the Sb-Cs cathode is by far the most sensitive type. Next in sensitivity is the Bi-O-Ag-Cs cathode, while the Ag-O-Cs cathode is approximately twenty times less sensitive than the Sb-Cs cathode. Daylight, as distinct from direct sunlight, has no well-defined emission spectrum [42] but, as is apparent from the blue colour of the sky, it always contains a greater percentage of short wavelength radiation than direct sun-



light, so that the outstanding sensitivity of the Sb-Cs cathode is even more pronounced.

(5) *Light sources of predominantly blue colour.* To this group belong several types of discharge tubes, in particular the low- and high-pressure Mercury lamps, and some of the fluorescent screens which are used in cathode-ray tubes. Obviously for all these sources the Sb-Cs cathode is by far the most sensitive. As an example, it may be stated that in the case of a blue fluorescent screen which, owing to its short afterglow, is used for cathode-ray tube scanning in television (see page 93), the Sb-Cs cathode is approximately 200 times more sensitive than the Ag-O-Cs cathode.

(6) *Sources of ultra-violet radiation.* The most important sources are Mercury and Hydrogen discharge tubes made of quartz or provided with a quartz window. Owing to the fact that even photocathodes of comparatively high work function are sensitive to ultra-violet radiation, a great number of types is available for this range of the spectrum, including pure metal cathodes. In the past the most frequently used types have been the Cadmium, Sodium and Ag-O-K cathodes. The more recently developed Sb-Cs cathode has proved to be several hundred times more sensitive than any of the above-named cathodes for wavelengths between 2,000 Å and 4,000 Å, so that in the future it will probably replace the other types completely. (Reliable and reproducible response curves for the ultra-violet range have not been published for any cathode. This is the reason why the curves in Figs. 9, 11 and 12 are not continued into the ultra-violet range of the spectrum.) A great additional advantage of the Sb-Cs cathode is that it can be used for the visible as well as for the ultra-violet range of the spectrum, whereas the other cathodes mentioned in this paragraph, owing to their greater work function, have a shorter threshold wavelength and are therefore not so suitable for the visible range.

(7) Finally, it must be mentioned that for several prac-

tical applications a cathode is required with a spectral response curve similar to that of the human eye (Fig. 15), i.e. a curve covering only the wavelength range from

4,000 Å to 7,600 Å and having a peak at approximately 5,500 Å. Up to date the closest, though by no means perfect, approximation to this requirement has been achieved with the Bi-O-Ag-Cs cathode. Previous to the development of

this cathode, the Ag-O-Rb cathode has been used to fulfil the same requirement. The response curves of both the Ag-O-Cs and the Sb-Cs cathodes, however, are unsuitable.

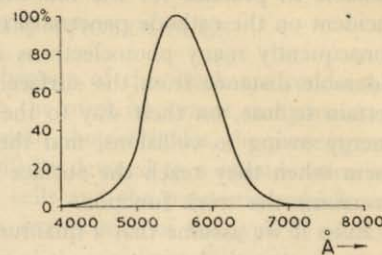


FIG. 15.—Colour response of human eye

#### (D) OUTLOOK FOR FUTURE DEVELOPMENTS

After having concluded the survey of the existing types of photocathodes it may be of interest to speculate what further improvements in photoelectric sensitivity can be expected in the future. We will consider this question briefly from the three following points of view. Firstly, what improvements in photocathodes are theoretically possible; secondly, what improvements are desirable, and thirdly, what improvements are likely to be achieved?

(1) The theoretical limit of sensitivity is represented by a quantum yield of 100% throughout the spectrum range in which we are interested, i.e. the range extending from 2,000 Å to 12,000 Å. As has been pointed out earlier, the highest quantum yield obtained in practice is the value of 20% for the peak sensitivity of the Sb-Cs cathode. In general, however, a quantum yield of 1% has been exceeded only in a few cases and only within limited wavelength ranges, so that an improvement by a factor of 100 and over is theoretically possible.



(2) The most desirable photocathode would, naturally, be a cathode with the theoretical maximum sensitivity, but it can be taken for granted that such a sensitivity is unobtainable in practice for the following reason. The light incident on the cathode penetrates to a certain depth, and consequently many photoelectrons are released at a considerable distance from the surface. These electrons are certain to lose, on their way to the surface, part of their energy owing to collisions, and the energy remaining to them when they reach the surface will be insufficient to overcome the work function.

Even if we assume that a quantum yield of 20% represents the practical maximum, it is still desirable for many practical applications to obtain response curves different from those of known cathodes. The following are two examples of desirable response curves: Firstly, if the peak of the Sb-Cs cathode could be shifted to 5,500 Å and the threshold wavelength to 8,000 Å, the sensitivity would approximate closely that of the human eye and, at the same time, would be very much increased for all practical thermal light sources. Secondly, if the peak could be shifted still further towards longer wavelengths the sensitivity to the light emitted by incandescent lamps would increase enormously.

(3) Concerning the practical possibilities of producing new types of cathodes with more useful characteristics, two general statements can be made. Firstly, it seems to be certain that any cathode of high sensitivity and low work function must contain the element Caesium. Secondly, all combinations of Caesium with one or two additional elements have been explored extensively, but no cathode of this type has been produced which is superior to the Ag-O-Cs and Sb-Cs cathodes. Therefore the prediction would seem to be justified that only combinations of Caesium with three or more additional elements are likely to yield cathodes of improved properties, the first example of this type being the Bi-O-Ag-Cs cathode.

## CHAPTER V

### VACUUM PHOTOCELLS

WHILE the previous chapters of this book are concerned almost exclusively with the most important component of photoelectric cells, i.e. with photocathodes, the present and subsequent chapters will be devoted to a consideration of complete photoelectric cells and the properties which are in common to all cells, irrespective of the type of photocathode used.

The simplest photoelectric cell is the vacuum cell which consists of an evacuated glass bulb containing the photocathode and the collecting anode. The most important characteristics of a vacuum cell are, firstly, the saturation voltage, i.e. the lowest positive anode potential at which all the photoelectrons released from the cathode are collected by the anode, and secondly, the frequency response.

#### (A) SATURATION POTENTIAL

In the ideal case the value for the saturation voltage is 0 volts because the initial velocity of the photoelectrons enables them to reach the anode without any further acceleration. The curves of Figs. 2 and 3 show a saturation voltage of 0 volts, and with the necessary precautions (concerning contact potentials, &c.) such curves can be obtained with experimental cells if the cathode is almost entirely surrounded by the anode. In cells for practical use this condition cannot be fulfilled because an anode which surrounds the cathode will prevent light from reaching the cathode; therefore a positive potential has to be applied to the anode in order to obtain saturation, but for practical reasons a low anode potential is usually desirable.

From the foregoing it is clear that vacuum cells have to be so constructed that the saturation voltage is reason-



ably low while at the same time the minimum amount of light is intercepted by the anode. This is frequently achieved by using a cathode of semicylindrical shape and an anode consisting of either a wire rod positioned at the axis of the cylinder or a rectangular wire frame as shown in Fig. 8; however, in practice a great number of different anode and cathode constructions are met because the application for which the cell is intended often determines the design.

Typical saturation curves obtained with cylindrical vacuum cells are shown in Fig. 16. The curves represent

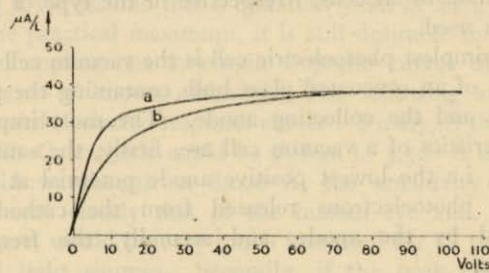


FIG. 16

the characteristics of two cells (a) and (b) of identical overall and cathode dimensions but differing in that cell (a) has a wire frame anode similar to that in the cell shown in Fig. 8, while cell (b) has only a short straight wire anode at one end of the bulb. According to expectation, cell (a) has the lower saturation voltage.

It should be emphasised that for most practical purposes a very low saturation voltage is not an essential requirement; therefore the anode design is comparatively unimportant provided the saturation voltage does not greatly exceed 100 volts.

#### (B) FREQUENCY RESPONSE

In many applications a photocell is used to detect light signals of very short duration, following each other in rapid

succession. The degree of accuracy with which the photocurrent in a cell reproduces such signals is a measure of the frequency response of the cell. The frequency response of the actual photoelectric emission is perfect because the photoelectrons are released instantaneously when light is incident on the cathode, and the electron emission ceases instantaneously when the illumination ceases. However, the frequency response of the photocurrent depends on the geometry of the cell and on the anode potential, as can be seen from the following consideration.

Owing to the fact that the transit time of the photoelectrons, i.e. the time the electrons require to move from cathode to anode, has a finite value, there always exists a small time lag between the emission of the electrons from the cathode and their arrival at the anode. If the frequency of the light signal is so high that the duration of a single light pulse is comparable with the transit time of the photoelectrons, the frequency response of the cell will no longer be perfect because the single photocurrent pulses will now be of longer duration than the light pulses which have caused the photocurrent, and therefore the photocurrent will be a distorted equivalent of the light signal. The frequency response is further reduced if, owing to the geometry of the cell, the transit times of electrons released from different parts of the cathode are not identical.

An example may show at what frequencies the transit time in a vacuum cell will affect the response.

If the cathode to anode distance is approximately 3 cm. and if the anode potential is 100 volts, the transit time of the electrons is of the order of  $10^{-8}$  seconds.\* Therefore in this particular case the frequency response is

\* This value is derived as follows: The transit time ( $t$ ) of an electron leaving the cathode with velocity 0 and arriving at the anode with the velocity ( $v$ ) is given by

$$t = \frac{2d}{v} \quad (6)$$



affected at frequencies above approximately  $10^7$  cycles per second. For larger distances and lower anode potentials the critical frequency is correspondingly lower.

where ( $d$ ) is the distance between cathode and anode. (This equation assumes uniform acceleration of the electrons and the results obtained from it are only strictly correct if cathode and anode are two plane parallel plates.) The final velocity ( $v$ ) is determined by the anode potential ( $V$ ) (measured in volts) according to the equation:

$$v = \sqrt{\frac{2e}{m} \times V} \quad (7)$$

in which ( $e$ ) is the electronic charge and ( $m$ ) is the mass of the electron. By substituting the numerical values for ( $e$ ) and ( $m$ ) we obtain from equations (6) and (7) the final equation for the transit time

$$t = \frac{2d}{5.93 \times 10^7 \sqrt{V}} \quad (8)$$

Hence for our example ( $d = 3$  cm. and  $V = 100$  volts) we obtain  $t = 10^{-8}$  sec.

## CHAPTER VI

### GASFILLED PHOTOCELLS

#### (A) MECHANISM OF GAS AMPLIFICATION

(a) *General.* The purpose of introducing gas into a photocell is to effect an amplification of the electron current emitted by the photocathode. This amplification is produced by the following physical process.

If a sufficient gas pressure is maintained within a photoelectric cell, the mean free path of the photoelectrons ejected from the cathode is reduced to such a small value that each electron is likely to collide on its way to the anode with one or more gas molecules. When such a collision takes place the electron is able to ionise the gas molecule, i.e. to split it into one positive ion and one electron, provided the velocity of the electron, expressed in volts, exceeds the ionisation potential of the gas. The values of the ionisation potentials of gases lie between 10 volts and 25 volts and the maximum velocity of the photoelectrons is equal to the potential applied to the anode of the cell (if we ignore the minute initial velocities of the photoelectrons which for visible light are always below 3 volts). Therefore ionisation by collision will take place in gasfilled cells having anode potentials of over 25 volts.

The positive ions produced as a result of the ionisation process are collected by the cathode of the cell and the original photoelectrons, together with the electrons produced as a result of the ionisation process, are collected by the anode. If each photoelectron ionises one gas molecule the total photocurrent is amplified by a factor of 2, because for each photoelectron released from the cathode a total of two electrons is collected by the anode.

A factor greater than 2 can be obtained if the anode potential is considerably larger than the ionisation potential of the gas. In this case three physical processes take place



simultaneously, all of which contribute to the amplification of the original photocurrent. These processes are:

(1) *Ionisation by multiple collisions of electrons with gas molecules.* If the anode potential exceeds twice but not three times the value of the ionisation potential of the gas it is possible for each original electron to acquire after one 'successful' collision sufficient energy for a second ionisation process by collision. Moreover, every electron released by a collision of a photoelectron with a gas molecule may ionise one additional gas molecule. If the anode potential exceeds three times or more the value of the ionisation potential a correspondingly greater number of ionisation processes is possible.

(2) *Ionisation by collision of positive ions with gas molecules.* In analogy to the ionisation by collision of electrons with gas molecules, the positive ions created by this ionisation are able, in their turn, to cause ionisation by collision with gas molecules, provided their energy exceeds the ionisation energy of the gas. Positive ions, in the same way as electrons, are able to cause more than one ionisation process, provided they acquire sufficient energy between two collisions.

(3) *Creation of electrons by secondary emission.* If positive ions impinge on the cathode with sufficient energy, they release secondary electrons which represent a further contribution to the gas amplification. The number of secondary electrons emitted depends on the energy of the positive ions and also on the ability of the cathode surface to emit secondary electrons.

As has been mentioned already, an amplification factor of two is to be expected in a gasfilled cell if the anode potential exceeds the ionisation potential of the gas and if each photoelectron ionises one gas molecule. If the anode potential is greater than twice the ionisation potential, it is apparent from the foregoing that enormous factors of amplification would be obtainable, provided all the collisions of the newly released electrons and positive ions with gas

molecules lead to ionisation. In reality, however, at all anode potentials only a fraction of the collisions contributes to the amplification of the primary photocurrent for the following reasons:

Firstly, if electrons or positive ions collide with a gas molecule before they have acquired sufficient energy they are unable to ionise the molecule, though they may lose part of their energy in the collision process. Secondly, a positive ion may collide with an electron, and vice versa, before reaching cathode or anode respectively; if this happens, 'recombination' is likely to take place and the ion and electron concerned will not contribute to the amplification process.

(b) *Effect of gas pressure and geometry on gas amplification.* If a photocell contains a gas of known ionisation energy the gas amplification at a fixed anode potential is determined by two factors, viz. the distance between cathode and anode and the gas pressure. The effect of these two factors on the amplification can be understood from the following considerations:

(1) If the gas pressure ( $p$ ) is kept constant and the anode-cathode distance ( $d$ ) is gradually increased, very few collisions will take place as long as ( $d$ ) is smaller than the 'mean free path' at the pressure ( $p$ ) because most photoelectrons will reach the anode before they have suffered a single collision. With increasing distance, more collisions and therefore more ionisation processes occur, but ( $d$ ) will eventually reach such large values that the energy imparted to the electrons and positive ions by the electric field between two collisions will not be sufficient in all cases to cause ionisation. It is, therefore, evident that an optimum value of ( $d$ ) exists for every value of ( $p$ ).

(2) If the distance ( $d$ ) is kept constant and the gas pressure ( $p$ ) is gradually increased, three stages can be distinguished in analogy to the considerations of the preceding paragraph. At small values of ( $p$ ), for which the 'mean free path' is greater than ( $d$ ), only very few collisions will take place,



With increasing pressure the number of collisions increases, but eventually ( $p$ ) will reach such large values that the electrons and positive ions will not acquire sufficient energy between two collisions in all cases to cause ionisation. In this last stage the gas amplification is still further reduced by the increasing number of recombination processes. In analogy to the previous paragraph it can be stated that an optimum value of ( $p$ ) exists for every value of ( $d$ ).

From the two preceding paragraphs the conclusion can be drawn that owing to the interdependence of ( $p$ ) and ( $d$ ) an optimum value of the product ( $p \times d$ ) exists for every anode potential. In practice the value of ( $d$ ) is usually determined by the requirements of the application for which the photocell is intended, so that it is necessary to adjust the gas pressure to the geometry of the cell.

(c) *Effect of anode potential on gas amplification.* As has already been mentioned, an increase of the potential applied to the anode of a gasfilled cell leads to an increase of the gas amplification because more charged particles are produced both by collision processes and by secondary electron emission from the cathode. However, the increase of the amplification factor obtained by increasing the anode potential is limited by the fact that above a certain anode potential (depending on gas pressure, cathode material, geometry of the cell, &c.) a self-maintained discharge starts within the cell and this does not stop when the irradiation of the photocathode, i.e. the emission of photoelectrons, ceases. Under these conditions the cell can no longer be called a photoelectric device because the current flowing to the anode is not controlled by the light incident on the cathode, and the characteristics of the cell are now those of a cold-cathode gasfilled diode.

#### (B) GASFILLED PHOTOCELLS IN PRACTICE

(a) *Nature of gas and gas pressure.* The number of suitable gases for use in gasfilled photocells is restricted for two reasons. Firstly, owing to the great chemical reactivity

of the Alkali metals present in all modern photocathodes, the choice is confined to the rare gases which are unable to form chemical compounds. Secondly, it is advantageous to use a gas which has a low ionisation potential and is therefore ionised at low anode potentials.

The values of the ionisation potential of the rare gases decrease with increasing atomic weight, i.e. from Helium to Xenon (see Table I). In practice, Argon is almost universally used for the gasfilling of photocells because the two gases of highest atomic weight, viz. Krypton and Xenon, are only available in very small quantities. In the remainder of this Chapter we shall assume that all gasfilled cells contain Argon.

The most suitable gas pressure in a gasfilled photocell is determined, as has already been explained, by the ionisation potential of the gas, by the geometry of the cell and by the available anode potential. Assuming normal working conditions, i.e. if cells of conventional geometrical design are used with anode potentials ranging between 80 volts and 200 volts, the optimum gas pressure lies in the case of Argon gas between 0.1 and 1.0 mm. Hg.

(b) *Current-voltage characteristics and glow discharge.* The effect of the anode potential on the gas amplification can be seen in Fig. 17, in which the sensitivities of three cells of identical cathode sensitivity and of identical dimensions are plotted against the anode potential. Curve (a) represents a vacuum cell and curves (b) and (c) represent gasfilled cells, the pressure in cell (b) being higher than in cell (c). From these three curves the following conclusions can be drawn.

(1) For anode potentials between 0 and approximately 20 volts the curves for the two gasfilled cells are identical with the curve for the vacuum cell. This is due to the fact that at anode potentials below the ionisation potential of Argon (15.7 volts) ionisation cannot take place.

(2) Above anode potentials of 20 volts curves (b) and (c) rise more and more steeply in accordance with the increasing



number of ionisation processes. Ultimately the curves approach the vertical, the anode potentials corresponding to this 'infinite sensitivity' indicating the potentials at which the self-maintained discharge begins.

(3) At all anode potentials above 20 volts the sensitivity, i.e. the gas amplification, of the cell with higher gas pressure (*b*) is greater than that of the cell with lower gas pressure (*c*). However, in cell (*b*) the self-maintained discharge begins at approximately 100 volts, while cell (*c*)

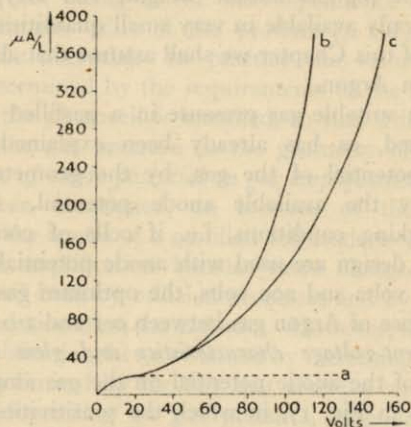


FIG. 17

is controlled by light up to approximately 140 volts. This means that for a given anode potential below 100 volts the gas pressure in cell (*b*) is nearer to the optimum value than in cell (*c*), but it can also be seen that if higher anode potentials are available the same sensitivity can be obtained with cell (*c*) as with cell (*b*) at the lower potential.

The phenomenon of the self-maintained discharge requires more detailed consideration in order that its bearing on the practical use of gasfilled photocells can be understood. If the anode potential of a gasfilled cell is gradually increased, self-maintained discharge will start at

a certain anode potential even if the cell is kept completely in the dark, i.e. if it is used purely as a gasfilled diode. This discharge is initiated by the few charged particles which are always present in gasfilled tubes. We will call the anode potential, at which the self-maintained discharge starts in a photocell when no light is incident on the cathode, the 'dark discharge potential'. This potential has a fixed value for each cell if we ignore minor variations common to all discharge tubes.

If the number of charged particles within a gasfilled diode is increased the anode potential at which a self-maintained discharge starts is reduced. Therefore, if light is incident on the cathode of a gasfilled photocell the self-maintained discharge will start at potentials below the 'dark discharge potential' because the charged particles responsible for the initiation of the 'dark discharge' are now augmented by photoelectrons. It is evident that the 'light discharge potential', in contrast to the 'dark discharge potential', has not a fixed value for every cell, because it will be of lower value if the cathode is exposed to stronger illumination, i.e. if the number of photoelectrons released per unit time is increased.

The change of 'light discharge potential' with illumination is of great importance in the practical use of gasfilled photocells because it means that the highest working potential that can be applied to a gasfilled cell must be lower than the 'light discharge potential' associated with the strongest illumination to which the cell may be exposed in use. In general it can be stated that with increasing number of primary photoelectrons the factor of gas amplification that can be safely used is reduced; therefore the highest factors can be obtained with cathodes of low sensitivity which are exposed to very weak illumination.

The following figures obtained with gasfilled cells when used for various applications will illustrate the practical range of amplification factors. (These figures refer to the



most sensitive photocathodes and would be correspondingly higher for less sensitive types.)

Factors of the order of 10 to 20 can be used for most general applications (for instance, sound reproduction). In cases where the maximum illumination is definitely limited to very small values (for instance measurement of the brightness of stars), working potentials corresponding to amplification factors of over 100 can be employed. On the other hand, in cases where very strong illumination is incident on the photocathode the maximum potential that can safely be applied to the anode may correspond to a factor of only 3.

The limitations set forth in the preceding paragraph can be expressed briefly by stating that the photocurrent in a gasfilled cell of conventional geometry must not exceed values of the order of 10 to 20 microamps. A corresponding definite upper limit for the working potential cannot be given because the critical 'light discharge potential' depends on the magnitude of the primary photocurrent so that the maximum safe working potential may lie between a fraction of a volt and 30 volts below the 'dark discharge potential'. It has, however, been found experimentally that at working potentials of more than 30 volts below the 'dark discharge potential' a self-maintained discharge cannot, as a rule, be produced even with the strongest illumination.

Referring again to the curves in Fig. 17, it can be seen that at the higher 'dark discharge potential' (curve (c)), i.e. at lower gas pressure, the curve rises less steeply than at the lower 'dark discharge potential' (curve (b)) so that, with the safety margin of 30 volts suggested above, greater amplification factors can be obtained with cell (c). If we assume a 'dark discharge potential' of approximately 120 volts for curve (b) and of approximately 160 volts for curve (c) (the value of the 'dark discharge potential' cannot be derived with accuracy from any curve based on measurements taken with illuminated cathode), the sensi-

tivities at 30 volts below the 'dark discharge potential' are 180  $\mu\text{A/L}$  for (b) and 240  $\mu\text{A/L}$  for (c), corresponding to amplification factors of 9 and 12 respectively.

In connection with the self-maintained discharge in gasfilled photocells a few remarks must be added concerning the visible glow that can be observed in such cells. While the self-maintained discharge in a photocell is always visible, a visible glow in a cell which is exposed to light does not necessarily mean that the working potential is too high, i.e. that it exceeds the 'light discharge potential'. By observing in complete darkness a gasfilled cell with an Ag-O-Cs photocathode which is exposed to infra-red radiation, it has been found [41] that, even at anode potentials only slightly above the ionisation potential of the gas and with comparatively small currents (1  $\mu\text{A}$ ), a glow is visible. This phenomenon means that the ionisation processes within the cell are accompanied by the emission of visible radiation. The glow disappears when the source of radiation is removed and can thus be distinguished from the glow accompanying the self-maintained discharge.

(c) *Frequency Response.* It has been pointed out in Chapter V that the frequency response of a vacuum cell can be considered perfect for most practical applications because the transit time of the photoelectrons is the only limiting factor. In contrast to the vacuum cell, the frequency response of the gasfilled cell falls off at comparatively low frequencies owing to the fact that several processes take place in the gasfilled cell which cause time lags of much greater magnitude than those due to the transit time of electrons. The following are probably the most important reasons for time lag in a gasfilled cell.

(1) Part of the photoelectric current flowing in a gasfilled cell is carried by positive ions which, owing to their mass, move with lower velocity than electrons. The velocity of charged particles is given by equation (7) (page 60), i.e. the velocity is inversely proportional to the root of the mass. Therefore the velocity of the ion in the case of



Argon, for instance, is almost 300 times smaller than that of an electron. Smaller velocity leads to larger transit time and correspondingly reduced frequency response. The calculated increase of transit time refers to a positive Argon ion moving undisturbed from anode to cathode; in reality, however, such an ion will suffer numerous collisions so that the transit time will be even further increased.

(2) Some collisions in gasfilled cells result in gas molecules attaining metastable states of excitation, i.e. states which may persist unchanged for comparatively long periods. Such metastable molecules are able to produce new charged particles by collisions which take place after the photoelectric emission from the cathode has ceased; the result of this effect is a further time lag between light signal and photocurrent.

(3) Positive ions arriving at the cathode after the photoelectric emission has stopped, release secondary electrons which, in turn, cause a current to flow to the anode and further collisions to take place and thus are a source of a still greater time lag.

All three effects will become more noticeable if the number of 'successful' collisions is increased, in other words, if the gas amplification factor is increased. As a result of the time lag the amplitude of the alternating component of the photoelectric current is reduced and this effect, i.e. the reduced frequency response, manifests itself in a reduction of the effective sensitivity to a.c. signals. Fig. 18 shows how the sensitivity of one particular gasfilled cell depends on the frequency of the light signal and on the amplification factor  $G$  [1]. The values are given as fractions of the sensitivity of a vacuum cell which is independent of frequency within the frequency range shown in the Figure. It can be seen from Fig. 18 that, working with an amplification factor of 10, the sensitivity of the gasfilled cell is reduced to approximately 50% at a frequency of 10,000 cycles.

(d) *Comparison of vacuum and gasfilled cell.* Vacuum cells and gasfilled cells are both extensively used in practice, and it is important to realise the relative advantages and disadvantages of the two types. The following is a short summary of the properties in which vacuum and gasfilled cells differ, based on the more detailed discussion in the preceding pages.

(1) *Sensitivity.* Gasfilled cells are always more sensitive than vacuum cells with the same photocathode, provided the anode potential is greater than 25 volts. The maximum

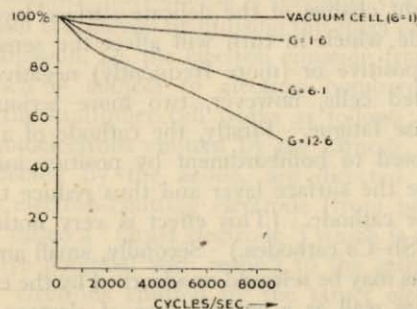


FIG. 18

factor of gas amplification that can be obtained decreases with increasing illumination so that the difference in sensitivity between gasfilled and vacuum cells is most striking in cases where only very little light is incident on the cell.

(2) *Effect of anode potential on sensitivity.* The sensitivity of a vacuum cell is independent of the anode potential provided the latter is higher than the saturation potential; even very high anode potentials (1,000 volts and over) do not harm the cell. On the other hand, the sensitivity of a gasfilled cell is a function of the anode potential so that this potential has to be kept absolutely constant if constant sensitivity is required. Moreover, if the anode potential exceeds at any time the value at which a self-maintained



discharge sets in, a gasfilled cell is no longer controlled by light and may be damaged.

(3) *Fatigue effects.* In connection with photoelectric cells it is advantageous to use the term fatigue for both negative and positive changes of sensitivity. We are mainly interested in any fatigue effect occurring while the photocathode is exposed to radiation and a positive potential is applied to the anode, i.e. while a photocurrent is flowing. Under these conditions both in vacuum and in gasfilled cells the actual process of electron emission may cause a slight change of the delicate surface layer of the photocathode which in turn will affect the sensitivity in either the positive or (more frequently) negative sense.

In gasfilled cells, however, two more serious effects tend to cause fatigue. Firstly, the cathode of a gasfilled cell is exposed to bombardment by positive ions which may damage the surface layer and thus reduce the sensitivity of the cathode. (This effect is very noticeable in the case of Sb-Cs cathodes.) Secondly, small amounts of the filling gas may be released or adsorbed by the electrodes and the glass wall as a consequence of electron and ion bombardment. If such an effect takes place the gas pressure is slightly altered and therefore the amplification factor, and consequently the sensitivity, is either increased (if gas is released) or reduced (if gas is adsorbed).

(4) *Frequency response.* The frequency response of the vacuum cell is practically perfect while the response of the gasfilled cell falls off noticeably at frequencies above approximately 1,000 cycles per second.

From the preceding paragraphs it is evident that the vacuum cell is superior to the gasfilled cell with regard to the properties discussed under headings (2), (3) and (4), while the advantage of the gasfilled cell lies in its higher sensitivity (heading (1)); hence the use of the gasfilled cell is confined to applications where neither great accuracy nor high-frequency response is required. This subject will be discussed in greater detail in Chapter VIII.

## MULTIPLIER PHOTOCELLS

## (A) GENERAL PRINCIPLES

THE demand for a photoelectric cell with internal amplification of the primary photoelectric current but without the limitations to which the gasfilled cell is subject, viz. low amplification factor and low frequency response, has led to the development of the multiplier photocell.

The multiplier photocell is a vacuum cell in which amplification is achieved by utilising the effect of secondary electron emission, i.e. the electron emission from an electrode which is subject to electron bombardment. In principle the multiplier cell works as follows:

The photoelectrons emitted by the cathode, instead of being collected by the anode, are directed towards a secondary electron-emitting electrode (from now on, for shortness, called a 'target electrode') which is maintained at a positive potential with respect to the cathode. The secondary electrons emitted by the target electrode can then be collected by an electrode serving as the anode which, of course, has to be at a positive potential with respect to the target electrode. If during the bombardment of the target electrode every photoelectron releases  $S$  secondary electrons, the original photocurrent is amplified by a factor  $S$ .

One great advantage of amplification by secondary emission as compared with amplification by gasfilling lies in the fact that the process of amplification can be repeated many times within the same cell, by making the electron stream impinge on a succession of target electrodes which are maintained at increasing positive potentials. The total multiplication factor  $M$  obtained with a multiplier cell is a function of the factor  $S$  of each electrode and of the number of target electrodes  $n$ , according to the equation

$$M = S^n \quad (9)$$



The multiplication factor  $S$  of a target electrode is determined mainly by the chemical nature of its surface and by the velocity with which the bombarding electrons strike the electrode. The factors governing the effect of secondary emission will be discussed more fully in the following section, not only because they are important for the understanding of the multiplier photocell but also because of the interesting relationship between secondary and photoelectric emission.

#### (B) SECONDARY EMISSION [29, 44]

A complete theory of secondary emission, particularly with regard to the mechanism of emission from the complex materials which provide the most efficient target electrodes, has not yet been developed, but a number of general conclusions can be drawn from experiments and from analogies with photoelectric emission.

If a bombarding electron, usually called a primary electron, of high velocity penetrates the surface of a target electrode, it imparts its energy to one or more electrons within the electrode; some of these electrons will leave the surface as secondary electrons or, if they have acquired sufficient energy from the primary electron, they will produce additional secondary (strictly speaking 'tertiary') electrons which in turn may release further electrons by transfer of energy. As a result of this 'splitting up' of the kinetic energy of the electron within the electrode, the secondary electrons emerge from the surface with a comparatively narrow velocity 'spectrum', i.e. the majority of the secondary electrons, produced by primaries of several hundred volts velocity, have velocities within the range of 0 to 30 volts. (It must be added, however, that a fraction of the primary electrons are reflected from the surface of the target electrode and therefore leave the surface with their original velocity.)

The general conditions for photoelectric emission on pages 10-16 apply also for secondary emission (except, of

course, the condition of light absorption), but, owing to the different sources of energy responsible for the two types of emission, the condition of low work function is not of such fundamental importance for secondary emission as it is for photoelectric emission.

While, as has been explained in Chapter II, the energy available for the release of a photoelectron by visible light cannot exceed 3 volts, in the case of secondary emission any amount of energy may be imparted to the primary electrons by applying to the target electrode a high positive potential with respect to the source of the primary electrons. Hence the choice of materials suitable for target electrodes is not limited, as is the case with photocathodes, by the condition that the work function must be lower than 3 volts, though, *ceteris paribus*, a substance of low work function will obviously be a more efficient emitter of secondary electrons than a substance of higher work function.

In accordance with the considerations set out in the previous paragraph, it has been found experimentally that all photocathodes have high secondary emission factors, while by no means all secondary electron-emitting electrodes with high secondary emission factor are photoelectrically sensitive to visible light. With target electrodes having photoelectric surfaces of the Ag-O-Cs, Ag-O-Rb and Sb-Cs types, secondary emission factors of the order of 10 and over have been obtained. On the other hand, with target electrodes consisting of a partially oxidised Silver-Magnesium alloy, which are not photoelectrically sensitive, secondary emission factors of almost equal magnitude have been measured [51].

The effect of the velocity of the primary electrons on the secondary emission factor is fundamentally similar for all types of target electrodes; the factor  $S$  increases, at first rapidly, with increasing velocity of the primary electrons to a maximum value and then decreases gradually. Fig. 19 shows the factor  $S$  plotted against the velocity of



the primary electrons for a target electrode of the Ag-O-Cs type. The fact that the factor  $S$  does not increase indefinitely with increasing velocity of the primaries is explained by the following consideration. With increasing velocity, the primary electrons will penetrate more and more deeply into the target electrode, so that ultimately some secondary electrons are produced at a great distance from the surface. These electrons are likely to lose so much energy on their way to the surface that they are not able to overcome the work function. The maximum of the curve in Fig. 19

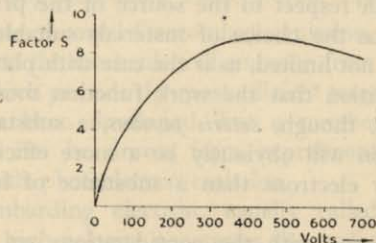


FIG. 19

indicates the potential at which this 'absorption' of electrons balances the increase in the number of secondary electrons due to the increased velocity of the primary electrons. One experimental proof of this explanation of the maximum in the curve is based on the fact that if, for the same target material, the primary electrons strike the target electrode at an angle of  $90^\circ$ , the maximum  $S$  factor is obtained at lower potentials than if the primary electrons strike the electrode at angles other than  $90^\circ$ , because the primary electrons at an angle of incidence of  $90^\circ$  will penetrate to a greater distance from the surface than if they are incident at an angle other than  $90^\circ$ .

#### (C) DESIGN OF MULTIPLIER PHOTOCELLS

For the efficient working of a multiplier photocell it is not only important to use electrodes having a high  $S$  factor,

but also to design the electrode system in such a way that full use is made of this factor, i.e. so that every electron emitted from one electrode is forced to strike the electrode forming the next stage in the succession of target electrodes. If some electrons by-pass one or more stages, as the result of the attracting force of an electrode at higher potential, the total multiplication factor of the cell is correspondingly reduced; it is therefore necessary to direct the electrons into certain paths through all stages of the multiplier system by applying either electromagnetic or electrostatic focusing. Of the very many suggested multiplier designs, only some of those that have been used

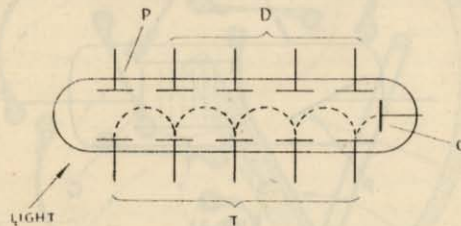


FIG. 20

P = Photocathode. D = Deflecting Electrodes. T = Target Electrodes.  
C = Collecting Electrode

in practice [27, 30, 35, 45, 46, 48, 50] will be described briefly in the following.

In the earliest multiplier photocells electromagnetic focusing [48] of the electron stream was used; an example of such a multiplier cell is shown in Fig. 20, which is self-explanatory. This design works with high efficiency but suffers from the disadvantage that the slightest change in the magnetic field alters the path in which the electrons move and consequently the multiplication factor. The working conditions with electromagnetic multipliers have proved so critical in practical use that in all modern multiplier cells only electrostatic focusing is employed.

Figs. 21 and 22 show diagrammatically the designs of



two types of multiplier systems in which the electron paths are controlled electrostatically by the geometry of the electrodes. In the multiplier shown in Fig. 21 the target electrodes consist of fine mesh grids [45], so that part of the electrons moving towards an electrode strike the wires of the mesh, while the remainder pass through the interstices towards the next electrode and are thus lost for the multiplication process. The advantage of this design lies in its simplicity, which makes it easy to increase the total multiplication factor  $M$  by adding more stages, but this simplicity is achieved at the expense of a low multiplica-

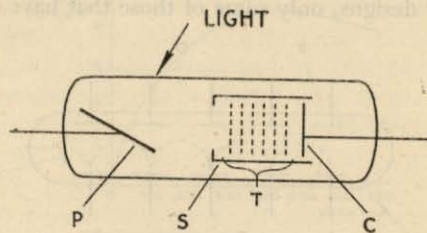


FIG. 21

P = Photocathode. S = Electrostatic Shield. T = Target Electrodes (Grids). C = Collecting Electrode

tion factor per stage. The factor  $S$  is only of the order of 2.5 if the electrodes are of the Ag-O-Cs type and if the potential difference between successive electrodes is 100 volts.

Fig. 22 shows the most efficient electrode system that has been developed up to the time of writing this book [27, 50]. Owing to the ingenious design of the electrodes,  $S$ -factors of the order of five are obtained, using a potential difference of 100 volts between successive stages of multiplication.

#### (D) CONSIDERATIONS CONCERNING THE PRACTICAL USE OF MULTIPLIER PHOTOCELLS

At first sight it would appear that the multiplier photocell is superior to the simple vacuum or gasfilled photocell in

every respect. However, the experimental work of the last ten years has demonstrated that only for certain applications do the advantages of using a multiplier cell outweigh the limitations to which it is subjected. In the following a brief survey will be given of the most important

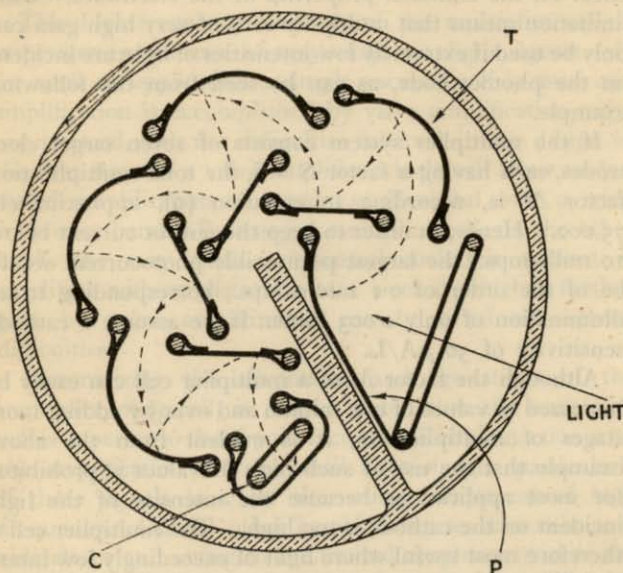


FIG. 22

P = Photocathode. T = 1st Target Electrode. C = Collecting Electrode

facts which determine the usefulness of the multiplier cell [40].

(a) *Economic considerations.* For many applications the cost of a multiplier cell, which is always much greater than that of a vacuum or gasfilled cell, may be prohibitive, whilst the requirement of a high-voltage supply for the target electrodes may prove a serious disadvantage.

(b) *Maximum output current and total multiplication*



*factor.* In all multiplier cells that have been developed to date the current collected after the last stage of multiplication, i.e. by the electrode having the highest positive potential, must not exceed 10 milliamps., mainly because the heat generated by larger currents has a detrimental effect on the emission properties of the electrodes. This limitation means that multiplier cells of very high gain can only be used if extremely low intensities of light are incident on the photocathode, as can be seen from the following example.

If the multiplier system consists of seven target electrodes, each having a factor  $S = 5$ , the total multiplication factor  $M$  is, according to equation (9), approximately 75,000. Hence, in order to keep the output current below 10 milliamps., the largest permissible photocurrent would be of the order of 0.1 microamps., corresponding to an illumination of only 0.003 lumen if we assume a cathode sensitivity of  $30 \mu\text{A/L}$ .

Although the factor  $M$  of a multiplier cell can easily be increased to values of one million and over by adding more stages of multiplication, it is evident from the above example that the use of such high  $M$ -values is prohibited for most applications because the intensity of the light incident on the cathode is too high. The multiplier cell is therefore most useful where light of exceedingly low intensity has to be detected. For the detection of very small a.c. signals the multiplier cell has the additional advantage that the 'signal-to-noise ratio' is low as compared with a simple vacuum cell followed by a valve amplifier [32].

(c) *Frequency Response.* The frequency response of a multiplier cell is slightly lower than that of a simple vacuum cell for the following reason: While in the simple vacuum cell the original photoelectrons move with increasing velocity from cathode to anode, in the multiplier cell the secondary electrons start with low initial velocity from each individual target electrode so that the total transit time from photocathode to collecting electrode is greater in the

multiplier cell than in the simple vacuum cell. This increase of the transit time does, however, in most cases not reach a factor of ten, so that, except for signals of very high frequency, the frequency response of the multiplier cell can be considered equal to that of the simple vacuum cell.

This high-frequency response of the multiplier cell is important in the case of very small a.c. light signals. If for such an application a simple vacuum cell is used and amplification is accomplished by valve amplification only, one is faced with the difficulties inherent in the design of the first stage of a valve amplifier which will allow undistorted amplification of a very small signal over a wide frequency band. By using a multiplier cell, on the other hand, the very small original photoelectric current is amplified without distortion to a level at which a further gain by valve amplification can be obtained without difficulties.

Summarising the advantages and limitations of the multiplier photocell, it can be stated that the multiplier cell is superior to the simple vacuum cell in connection with the amplification of very small light signals, particularly if these signals have an alternating component of high frequency. On the other hand, owing to economic considerations and owing to the limited output current of the multiplier cell, the use of a simple vacuum or gasfilled cell is indicated for applications where the incident illumination is sufficiently strong or where only response to d.c. or low frequency signals is required. Practical examples of the use of multiplier cells will be mentioned in the following Chapter.



## APPLICATIONS OF PHOTOCELLS

## (A) GENERAL

THE applications of photoelectric cells, particularly for industrial purposes, have become so numerous in recent years that a full description would require a book many times the size of this monograph. We shall therefore confine ourselves in the present Chapter to a discussion of the general principles underlying the practical use of photocells and to giving some examples of the different types of applications, without describing any particular application in detail.

The basic circuit in which the photocell is used in practically all applications is shown in Fig. 23 and consists of a

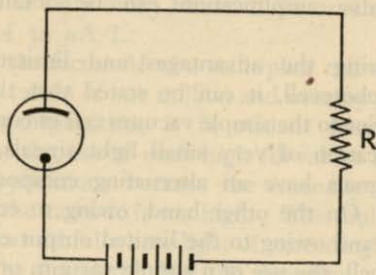


FIG. 23

voltage supply, photocell and resistance  $R$  in series. In the simplest practical case the resistance  $R$  is the internal resistance of a current-indicating instrument, for instance a galvanometer (Fig. 24). Alternatively,  $R$  may be the input resistance of a d.c. or a.c. valve amplifier (Fig. 25). From this latter circuit a great number of more elaborate radio circuits have been developed which are adapted to the particular application of the photocell. However, the problems of circuit design in connection with photocells constitute

a branch of radio and general electrical engineering and are outside the scope of this monograph. We shall therefore

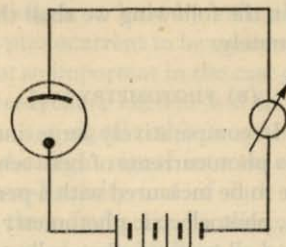


FIG. 24

consider in the present Chapter only the problems connected with the actual photocell as distinct from the electrical circuit of which the cell forms a part.

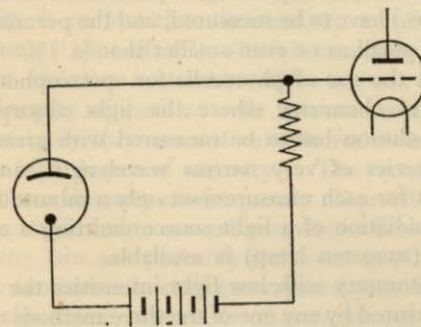


FIG. 25

For a general survey it is useful to subdivide the applications of photocells into the following three groups:

- (1) Definite fixed intensities of radiation have to be measured (Photometry).
- (2) Variations of light intensity have to be reproduced without distortion.
- (3) Relatively large changes in light intensity have to be detected.



In each one of these groups the photocell has to fulfil certain requirements which are not necessarily essential for the two other groups. In the following we shall therefore consider each group separately.

### (B) PHOTOMETRY [34]

(a) *General.* If comparatively large intensities of light (corresponding to photocurrents of between  $10^{-7}$  amps. and  $10^{-5}$  amps.) have to be measured with a permissible error of more than  $\pm 5\%$ , photoelectric photometry does not present any difficulties and all types of photocells can be considered suitable. The photocurrent in this case is, as a rule, measured by means of a galvanometer as indicated in Fig. 24.

However, in many modern applications, extremely low light intensities (corresponding to photocurrents of less than  $10^{-11}$  amps.) have to be measured, and the permissible error is often as small as or even smaller than  $\pm 1\%$ . A typical example is the use of photocells for spectrophotometry in biology and chemistry where the light absorption of a coloured solution has to be measured with great accuracy within a series of very narrow wavelength ranges; this means that for each measurement only a minute fraction of the total radiation of a light source emitting a continuous spectrum (tungsten lamp) is available.

For photometry with low light intensities the photocurrent is measured by any one of the three methods mentioned on page 82, viz. by a very sensitive galvanometer (useful down to approximately  $10^{-9}$  amps.) or by d.c. or a.c. valve amplification. (In the latter case the original d.c. light signal has to be converted artificially into an a.c. signal, e.g. by means of a 'chopper disc' interrupting the light beam at a convenient frequency.) In order to measure light intensities accurately it is essential that the photoelectric response of the cell is strictly linear, i.e. that the photocurrent is strictly proportional to the intensity of the light. Furthermore, if the light intensities to be measured are very

small, it is essential that the dark current, i.e. the current flowing between cathode and anode when the cathode is not exposed to radiation, is at least by a factor of ten smaller than the smallest photocurrent to be measured. (The latter requirement is not so important in the case of a.c. amplification because a steady dark current will in this case not be amplified with the a.c. signal; this is one of the advantages of converting a d.c. light signal into an a.c. light signal.) The causes of non-linearity and of dark current and the means by which these faults can be eliminated or reduced will now be discussed more fully.

(b) *Linearity of Response.* There do not exist any theoretical considerations or experimental results which would justify the assumption that the photoelectric current in a vacuum cell is not strictly proportional to the intensity of the incident radiation, except in the extreme case where the intensity is so low that the random emission of the photoelectrons ('shot effect'), which is caused by statistical fluctuations, becomes noticeable. (We are not concerned with the linearity of gasfilled cells because owing to their relative instability they are not suitable for measurements requiring a high degree of accuracy.) The fact that slight deviations from linearity are frequently observed in photocells can be attributed to several secondary effects of which the following two are probably the most important [8].

(1) If the anode area is small as compared with the cathode area, as is the case in most cells of conventional construction, some of the photoelectrons released from the cathode may strike the glass wall of the cell. Provided the anode potential is sufficiently high the photoelectrons will strike the glass wall with such velocities that they are able to release from the glass secondary electrons which are ultimately collected by the anode. The number of secondary electrons thus released is not proportional to the primary photocurrent because the glass, being an insulator, assumes a potential which is not uniform over the surface and is variable in time. Consequently the original photocurrent



will be augmented by a varying and undefined secondary electron current which will make the response of the cell appear non-linear.

(2) A slight non-linearity effect may be introduced by occasional collisions of photoelectrons with the gas molecules which are present even in the highest vacuum that can be obtained in practice. If these collisions lead to ionisation, i.e. if the anode potential is higher than the ionisation potential of the gas, an irregular increase of the photocurrent owing to gas amplification may occur.

These two effects responsible for non-linearity can largely be eliminated by suitable geometrical design of the photocell. As has been mentioned, both secondary emission from the glass wall and gas amplification are only possible if the anode potential is sufficiently high, i.e. if it is greater than approximately 20 volts. Hence, if the cell can be used with an anode potential of 20 volts or less, in other words, if the geometry of the cell is such that saturation is reached below 20 volts, then the non-linearity effect should disappear. A low saturation voltage has been achieved in practice by various geometrical designs, e.g. by surrounding the cathode with an anode made of wire mesh; the response of cells having such a construction (necessitating the use of a solid metal cathode as shown in Fig. 7, page 23) has been found to be strictly linear.

(c) *Dark current.* Dark current in a photocell can be due to two causes, firstly, internal or external electrical leakage between cathode and anode, and secondly, thermionic emission from the cathode. The two can easily be distinguished by the fact that the thermionic emission disappears if the cathode is made positive with respect to the anode.

The leakage current does not present a difficult problem because it can be reduced to values of less than  $10^{-12}$  amps. (at an anode potential of 100 volts) by employing suitable precautions. The main requirement is that the leakage path between cathode and anode should be made as great as possible, internally as well as externally. For instance,

in cells used for photometry the cathode terminal should always be as far as possible away from the anode terminal.

The thermionic emission from photocathodes seriously limits the exact measurement of very small light intensities if this emission at room temperature is of the same magnitude as, or even larger than, the photoelectric emission. It is therefore important to investigate how the thermionic emission can be reduced to a minimum. The thermionic emission of a photocathode, as that of any electron emitting substance, is determined by the following factors:

(1) The thermionic emission increases with a high power of the temperature. It can therefore be reduced most efficiently by cooling the photocathode; this is, however, rarely done in practice owing to the inherent technical difficulties.

(2) The total thermionic emission of a photocathode is proportional to the cathode area. Therefore the cathode area of a photocell used for photometry should not be appreciably larger than the area of any light spot incident on the cathode during use.

(3) The thermionic emission from a surface of low work function is larger than that from a surface of higher work function if the surfaces are at the same temperature. For this reason photocathodes with short threshold wavelength (high work function) show less thermionic emission at room temperature than photocathodes with longer threshold wavelength (lower work function). Of all known photocathodes, the Ag-O-Cs cathode has the longest threshold wavelength and is therefore unsuitable for photometric work at low light intensities, unless infra-red radiation, to which no other photocathode is sensitive, has to be measured. As examples of thermionic dark currents which have been actually measured it may be mentioned that the thermionic dark current at room temperature in the case of the Ag-O-Cs cathode is approximately  $10^{-9}$  amps. per square centimetre of cathode area, but in the case of the Sb-Cs cathode only approximately  $10^{-13}$  amps. per



square centimetre. (In passing it should be mentioned that for spectrophotometry the Sb-Cs cathode has the additional advantage of being most sensitive to the blue range of the spectrum, thus compensating for the low light intensity in this range of the spectrum if the light source is a tungsten lamp.)

(d) *Summary.* Summarising the considerations governing the use of photoelectric cells for photometry, the following points have to be borne in mind if results of high accuracy are required. The last two points are only of importance if the light intensity is extremely low.

- (1) Only vacuum cells should be used because of their greater stability as compared with gasfilled cells.
- (2) The geometry of the cell should be such that the saturation potential does not exceed 20 volts.
- (3) The internal and external leakage paths between cathode and anode should be as large as possible.
- (4) In order to reduce thermionic dark current, photocathodes of low work function, in particular the Ag-O-Cs cathode, should not be used. If there is a noticeable thermionic dark current the ambient temperature should either be lowered or, if this is not practicable, it should be kept constant to avoid variations of the dark current.

For measuring comparatively large light intensities or for measuring with a low degree of accuracy, practically any type of photocell can be used.

#### (c) REPRODUCTION OF RAPIDLY VARYING LIGHT INTENSITIES

The ability of the photocell to respond without distortion to variations of light intensity up to very high frequencies is the basis of such important applications as sound film reproduction, picture telegraphy and television where an accurate reproduction of the light signal is essential; these applications will form the subject of the following pages.

(a) *Sound film reproduction.* The task of the photocell in

sound film reproduction is to obtain from the variations in light transmission of the 'sound track' electrical pulses of equivalent amplitude and frequency, this being accomplished by passing the track between a constant light source and a photocell. The electrical pulses produced in the cell are used to modulate a loud speaker, after suitable amplification by a valve amplifier.

The maximum light flux to which the photocathode is exposed in this application, i.e. when the light passes through a clear section of the 'sound track', is of the order of 0.03 lumens, but obviously the cell has to respond to light intensities representing only a small fraction of this value when the light passes through dense parts of the track. It has been found in practice that, if a vacuum photocell is used, the output at low light levels is so small and, consequently, the amount of valve amplification required so great that the unavoidable microphonic noise originating from the first valve of the amplifier becomes excessive. For this reason gasfilled cells have been used universally for sound reproduction up to the present time.

The comparatively poor response of the gasfilled cell to frequencies above approximately 10,000 cycles per second (see Fig. 18), which are still within the audible frequency range, does not affect the quality of the sound in present-day projection equipment because the system by which the sound is originally recorded on the film does not in most cases respond to frequencies above approximately 8,000 cycles per second, and this limited recording response therefore represents the limiting factor. However, with further improvement in recording technique it may eventually become necessary either to use gasfilled cells with lower gas amplification, and consequently improved frequency response, or multiplier cells.

With regard to the photocathode in photocells used for sound reproduction, it can be stated that the Ag-O-Cs cathode has proved most successful because it is not liable



to deteriorate in gasfilled cells, in contrast to the Sb-Cs cathode (see page 72).

(b) *Picture Telegraphy and Television.* The basic principle of electrical picture transmission is the transformation of a picture, the brightness of which varies in two dimensions in space, into electrical signals, the amplitude of which varies in time. To accomplish this transformation, the picture is divided into a great number of individual picture elements and then 'scanned', i.e. the individual light values of each element are converted by means of a photoelectric cell into equivalent electric pulses which follow each other in rapid succession. Picture telegraphy and television differ in that the scanning of the still picture which has to be transmitted in picture telegraphy can be carried out at any convenient comparatively slow speed, while in the case of television each picture, whether still or moving, has to be scanned in a small fraction of a second ( $1/25$ th second or less) to avoid the effect of 'flicker' in the picture at the receiving end and, in the case of a moving picture, to allow rapid movement to be followed.

A picture that has to be telegraphed is usually scanned by moving it, point by point and line by line, in front of a fixed light spot. According to whether the picture is transparent or opaque, the light transmitted or reflected by each scanned picture element falls on the cathode of a photocell. The intensity of the light incident on the cell is so low that gasfilled cells are generally used, the cathode being of the Ag-O-Cs type, for the reason pointed out in connection with sound film reproduction. The frequency response of the gasfilled cell is sufficient for the scanning speed used in picture telegraphy.

The scanning of a television picture [52] represents a much more difficult problem because of the enormous scanning speed which is required to produce a picture of high definition without 'flicker'. In all modern transmission systems more than five million picture elements are scanned every second, so that the frequency response of the photo-

electric 'pick-up' device has to extend into the megacycle range. Consequently only vacuum cells are suitable for television transmission.

Before discussing the different types of photoelectric 'pick-up' tubes that have been developed for television transmission, we shall consider briefly the choice of the most suitable photocathode which, in most cases, is independent of the particular type of tube used. For the transmission of monochrome film or monochrome still pictures the colour response of the photocathode is immaterial. For the transmission of coloured studio or outdoor scenes, which are received on a cathode-ray tube in black and white, it is important that the colour response of the photocathode of the cell does not differ radically from the colour response of the human eye, because otherwise the distribution of dark and light will be distorted in the received picture. Finally, for transmission of a coloured picture which is also received in colour (colour television), it is essential that the photocathode should resemble the human eye in its colour response unless more than one cell is used, each cell having a photocathode of different colour sensitivity.

From the foregoing it is evident that the Ag-O-Cs photocathode, having maximum sensitivity to infra-red radiation and being comparatively insensitive to visible light (see Fig. 9), is not particularly suitable for televising objects other than monochrome film or still pictures. The use of the Ag-O-Cs cathode is still further restricted by its high thermionic emission at room temperature. This high thermionic emission means that the thermionic dark current is likely to be of the same order as the photocurrent because the latter is, as a rule, extremely small in television tubes. The Sb-Cs photocathode, having a much lower thermionic emission than the Ag-O-Cs photocathode and having also a more favourable colour response, has proved very successful for the transmission of both films and out-door scenes, provided monochrome reception is used. For colour television, however, the sensitivity of the Sb-Cs photocathode



to red light is inadequate (see Fig. 11) and the Bi-O-Ag-Cs photocathode is more suitable because it resembles the human eye most closely in its colour response (see Fig. 12).

The scanning of a picture which is to be televised can be effected by two fundamentally different methods. The first is similar to that used in picture telegraphy, i.e. the picture is scanned by a light spot and the reflected or transmitted light falls on the cathode of the photocell. According to modern applications of the second method an image of the picture to be televised is projected by means of an optical system on to a photoelectric surface and the resulting 'electron image' is scanned electronically. (The expression 'electron image' will be explained on page 93.) It is evident that the first method is limited to cases where it can be arranged that no light excepting the scanning light spot is incident on the object to be televised and is therefore only suitable for cinematographic film transmission and for use in a darkened studio, as distinct from the transmission of outdoor scenes or performances in a lighted studio.

In the following, the principles of four different television transmission systems will be outlined very briefly to illustrate the photoelectric problems arising in television transmission. The first two systems are based on the first of the above-mentioned methods and the other two are based on the second method.

(1) *Mechanical spot light scanning.* A light spot of great intensity scans the object to be televised either through the holes of a rapidly rotating disc (e.g. 'Nipkow disc') or by means of a mirror drum system, the holes or mirrors and the optical system being arranged in such a way that only one picture element of the object is illuminated at a time. The light reflected point by point from the object is incident on the cathode(s) of one or more photoelectric cells. It is advantageous to use cells of very large cathode area for this purpose because the light reflected by the object is diffused, which means that the amount of light 'collected' by the cathode, and hence the photocurrent, will increase with

increasing cathode area. The performance is still further improved by using a multiplier photocell.

It should be mentioned here that television is the ideal field for the use of multiplier cells because response to light signals of very high frequency and of extremely low intensity (owing to the small size of the individual picture element) is required. As has been pointed out on page 81, these are the conditions under which the multiplier cell is definitely more efficient than the simple vacuum cell.

(2) *Cathode-ray tube scanning.* Cathode-ray tube scanning is the electronic equivalent of the mechanical system described in the preceding paragraphs and has been developed in order to obtain scanning speeds which are not practicable in a mechanical system. In cathode-ray tube scanning the moving light spot is produced on the fluorescent screen of a cathode-ray tube by scanning this screen with a sharply focused electron beam. As in the case of mechanical scanning, the most suitable photocell for cathode-ray tube scanning is a multiplier cell with large photocathode. The fluorescent screens of cathode ray tubes generally employed for light spot scanning emit a high percentage of blue light, the reason being that the troublesome effect of 'afterglow' seems to be less marked in screens with blue fluorescence than in screens emitting light of longer wavelength. For cathode-ray tube scanning it is therefore essential to use a photocell with an Sb-Cs cathode.

(3) *The Image Dissector* [14]. We come now to the scanning systems in which the entire picture to be televised is projected on to the photocathode. In the case of the Image Dissector (see Fig. 26) the picture is projected on to a plane photocathode (*P*), from which it releases photoelectrons, forming an 'electron image'. This is the name given to an electron beam of large cross-section in which the electron concentration at each point is proportional to the brightness of the equivalent point of an optical image. By applying rapidly changing electromagnetic fields, the 'electron image' produced in the Image Dissector is moved, point



by point and line by line, across a minute hole in a metal plate (*S*) behind which the anode (*A*) is located. In this way at any given moment only the photoelectrons corresponding to one individual picture element are passing through the hole to be collected by the anode or, expressed more briefly, the 'electron image' is scanned.

The photoelectric cathode of the Image Dissector has to be very uniform in sensitivity over its whole area to ensure that the 'electron image' corresponds exactly to the optical image projected on to the cathode. This is in contrast to

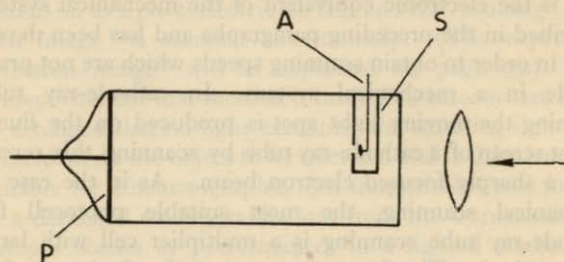


FIG. 26

the spot-light systems where for each picture element the total photoelectric emission of a constant cathode area is used, so that non-uniform cathode sensitivity does not cause any distortion of the received picture. The usefulness of the Image Dissector is considerably improved by using a multiplier system directly behind the scanning hole instead of an anode. But even so, the number of photoelectrons, emitted by the area of the cathode corresponding to one picture element, is so small that the Image Dissector cannot always be used reliably for the transmission of outdoor scenes where the available amount of illumination is often low. For the transmission of film, however, the intensity of the light source can be increased to a level at which the sensitivity of the Image Dissector is adequate to produce a satisfactory television picture.

(4) *Tubes of the Iconoscope type.* The inherent disadvantage of all television systems mentioned so far resides in the fact that only an extremely small number of photoelectrons is emitted per picture element, irrespective of whether the picture is scanned by a light spot or whether an 'electron image' is scanned electronically, and that consequently a strong light source is essential to produce a television picture of satisfactory 'signal-to-noise ratio'. This limitation has been overcome by the development of television transmission tubes in which use is made of the so-called storage principle. Whereas in all earlier systems the electrical signal due to one picture element consists only of the photoelectrons emitted during the very short time during which this particular element is being scanned, according to the storage principle the positive charge due to the emission of photoelectrons is 'stored' on each element of the photocathode during the whole period between two consecutive scanning processes.

It is evident that in the case of theoretically ideal 'storage' the signal resulting from one picture element should be greater than in the earlier systems by a factor equal to the total number of elements per picture, i.e. in the case of high definition television, by a factor of several hundred thousand. It may be mentioned here that up to the present time only factors representing a fraction of the ideal value have been obtained in practice.

The storage principle was for the first time successfully applied in the Iconoscope [47] a diagrammatic sketch of which is shown in Fig. 27. The Iconoscope does not contain a photocathode in the conventional sense but a large number (several times the number of picture elements) of very small photoelectrically sensitive particles (*E*), deposited on a thin plate of insulating material (*I*), usually mica. On the back of the insulating plate a continuous metallic layer (*M*) is deposited which is connected to a lead-in wire. Each photoelectric particle (*E*) thus represents one plate of a small condenser, the insulator (*I*) forming the dielectric



and the continuous metal layer ( $M$ ) forming the second plate of the condenser.

According to the original conception, if a picture is projected on to the photoelectric 'mosaic' each element will emit photoelectrons corresponding to the intensity of the incident light and will therefore charge up to a gradually increasing positive potential. The mosaic is scanned, point by point and line by line, by an electron beam (emanating from the electron 'gun' ( $G$ )) which neutralises

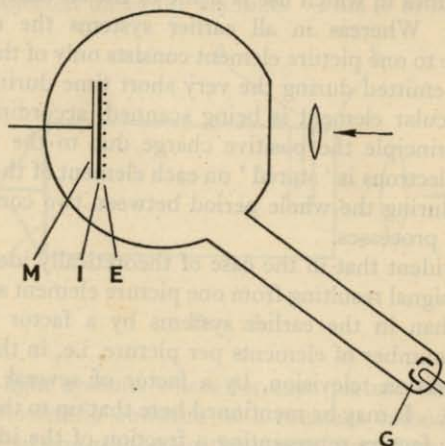


FIG. 27

the positive charges on the mosaic elements one by one and, by so doing, imparts electrical pulses to the metal layer ( $M$ ). These pulses are fed into a valve amplifier and the mosaic elements are ready again for the next charging and discharging cycle.

Unfortunately, experiments have shown [25, 49] that the mechanism described above represents an ideal which is not achieved in practice. The cycle of charging the mosaic by light and discharging it by electrons is seriously upset by the fact that the scanning electron beam releases secondary

electrons from the photoelectric elements and therefore the elements are positively charged after each scanning sweep. In consequence, the mechanism by which the Iconoscope works is much more complicated than would appear from the simplified explanation given in the preceding paragraph. The storage effect is very incomplete and a number of secondary effects cause distortions of the signal which have to be corrected in the electrical circuits. These problems are outside the scope of this monograph, but it must be mentioned that the faults of the Iconoscope have been reduced or overcome in storage tubes which have been developed from the Iconoscope and are known by the names of 'Super Emitron' [31] (or 'Image Iconoscope' [26]) and 'Orthicon' [36, 37]. In the latter the scanning electrons are of such low velocity that secondary emission cannot take place.

Regarding the Iconoscope as a photoelectric device, the novel problem of making a photoelectrically sensitive mosaic has to be solved. One usual method of producing a mosaic, consisting of sufficiently small particles, is to subject a continuous thin layer of Silver to heat treatment at approximately  $600^{\circ}\text{C}$ . At this temperature the Silver layer breaks up spontaneously into small individual particles. Such a Silver mosaic can then be used as the base layer of an Ag-O-Cs cathode. Up to date no method has been described by which a mosaic of the Sb-Cs type can be made, though such a mosaic would be superior to the Ag-O-Cs mosaic in colour response (see page 91).

Apart from the problem of producing the mosaic itself, it is more difficult to obtain high sensitivity with a photoelectric mosaic than with a continuous photocathode because the change of sensitivity of the insulated particles cannot be measured during the 'sensitising' process except by indirect methods. Furthermore, the sensitivity of the mosaic must be very uniform over its whole area for the reason given in connection with the Image Dissector.



#### (D) DETECTION OF RELATIVELY LARGE CHANGES OF LIGHT INTENSITY

Under this heading fall the majority of industrial applications of the photoelectric cell, but we can deal with the subject very briefly because the problems connected with this type of application are mainly circuit problems and do not concern the actual photocell.

The principle on which the applications considered in this section are based is as follows: a change of intensity, or of colour, of the light incident on the cathode of a photocell causes a change in photocurrent which, after amplification by a valve amplifier, controls (i.e. operates or releases) a relay. This relay may be used for a great number of purposes, e.g. to work a visual or audible alarm, to start a motor, to work an automatic counter, &c. To illustrate the variety of such applications, here are a few examples chosen at random: automatic door openers, burglar alarms (in both cases infra-red radiation in combination with the Ag-O-Cs photocathode is used), cigarette-counting, rejection of discoloured articles in production, mains voltage stabilisation, automatic opening and closing of camera shutter, &c. &c.

Concerning the choice of a suitable photocell for use in connection with relays, it can be stated that, as a rule, the demands made on the cell are not so exacting as in the case of photometry, television, &c. Gasfilled cells with Ag-O-Cs cathode are generally used, except for applications where a definite colour response is required, which necessitates the use of a different type of cathode. It must be emphasised that, whatever type of cell is used, the photocurrent is not large enough to work a relay without at least one stage of valve amplification.

#### (E) COMPARISON OF EMISSION CELLS AND BARRIER-LAYER CELLS

Although the theory, properties and manufacture of photocells of the barrier-layer type are not considered in

this monograph, a Chapter dealing with photocell applications would not be complete without referring briefly to the relative advantages and disadvantages of emission and barrier-layer cells.

The main advantage of the barrier-layer cell (apart from economic considerations), as compared with the emission cell, resides in the fact that it produces its own e.m.f., and accordingly can be used in series with a current-measuring instrument without the need for a voltage supply. For this reason the barrier-layer cell is particularly suited for mobile light-measuring instruments, the best known application being the photographic exposure-meter. A second advantage of the barrier-layer cell is that at high light levels it is able to energise very sensitive relays directly, i.e. without valve amplification.

On the other hand, the barrier-layer cell is inferior to the emission cell in two important properties. Firstly, its internal resistance is so low that it is difficult to use it in combination with valve amplification. Secondly, its frequency response is so low that it can be used neither for high-quality sound reproduction nor for high definition television.

#### (F) SUMMARY

For easier reference, the considerations which determine the choice of the most suitable photocell for a particular application are summed up in the following Table. In cases where more than one type of cell or photocathode is mentioned in the Table for the same application, the most suitable type is named first.



TABLE V

Application	Type of photo-cell used	Type of photo-cathode used	Remarks
Photometry high light intensity	barrier-layer cell		
	vacuum cell gasfilled cell	{ Ag-O-Cs Sb-Cs Bi-O-Ag-Cs	
low light intensity (great accuracy not required)	gasfilled cell	{ Ag-O-Cs Sb-Cs Bi-O-Ag-Cs	
	vacuum cell multiplier cell	{ Ag-O-Cs Sb-Cs Bi-O-Ag-Cs	
low light intensity (great accuracy required)	vacuum cell	{ Sb-Cs Bi-O-Ag-Cs Ag-O-K	special design to ensure low saturation potential and high insulation between cathode and anode
	multiplier cell		
special cases : infra-red radiation ultra-violet radiation		Ag-O-Cs	quartz window essential
		Sb-Cs	
Sound film reproduction	gasfilled cell	Ag-O-Cs	
	vacuum cell multiplier cell	Sb-Cs	
Picture telegraphy	gasfilled cell	Ag-O-Cs	
	vacuum cell	Sb-Cs	
Television spotlight scanning (mechanical or cathode ray tube)	multiplier cell	Sb-Cs	for film and (limited) studio use only
	vacuum cell		
special pick-up tubes	Image Dissector *	{ Sb-Cs Ag-O-Rb Ag-O-Cs	* for film and (limited) studio use only
	Iconoscope Super Emitron Orthicon		
For use in combination with relay high light intensity	barrier-layer cell		
	vacuum cell	Ag-O-Cs	
low light intensity	gasfilled cell	Ag-O-Cs	
	vacuum cell	{ Sb-Cs Ag-O-Cs	

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With regard to applications of photoelectric cells, the reader is referred to the books by ZWORYKIN and WILSON [2] and by WALKER and LANCE [5] for work carried out prior to 1937. The publications during the last eight years have been so numerous that a representative bibliography cannot be attempted in the available space. Most of the papers dealing with the applications of photoelectric cells have been published in the following journals: *Electronics*, *Electronic Engineering*, *Journal of Scientific Instruments* and *Review of Scientific Instruments*.

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